M. P., Osler, M. J. & Weyant, R. G.) 55-75 (Wilfrid Laurier University Press, Waterloo, 1980).
39. Cooper, D. E. in *Philosophy and Psychical Research* (ed. Thakur, S. C.) 59-80 (Allen & Unwin, London, 1976).
40. Scriven, M. in *Philosophy and Psychical Research* (ed. Thakur, S. C.) 181-194 (Allen & Unwin, London, 1976).
41. Wolman, B. J. (ed.) *Handbook of Parapsychology* (Van Nostrand, New York, 1977).
42. Beloff, J. *Zetetic Scholar* **6**, 90-94 (1980).
43. Morris, R. L. *J. Am. Soc. psychical Res.* **74**, 425-443 (1980).
44. Akers, C. in *Advances in Parapsychological Research* Vol. 4 (ed. Krippner, S.) 112-164 (McFarland, Jefferson, North Carolina, 1984).
45. Hyman, R. *J. Parapsychol.* **49**, 3-49 (1985).
46. Targ, R. & Puthoff, H. E. *Nature* **252**, 602-607 (1974).
47. Marks, D. F. & Kammann, R. *Nature* **274**, 680-681 (1978).
48. Hyman, R. *Skeptical Inquirer* **9**, 125-145 (1984-5).
49. Tart, C. T., Puthoff, H. E. & Targ, R. *Nature* **284**, 191 (1980).
50. Marks, D. F. *Skeptical Inquirer* **6**, 18-29 (1982).
51. O'Keefe, D. *Stolen Lightning* (Robertson, Oxford, 1982).
52. Wilson, S. C. & Barber, T. X. in *Imagery: Current Theory, Research and Application* (ed. Sheikh, A. A.) 340-387 (Wiley, New York, 1983).
53. Marks, D. & McKellar, P. *J. mental imagery* **6**, 1-124 (1982).
54. Gurney, E. & Myers, F. W. H. *Proc. Soc. psychical Res.* **5**, 403-485 (1889).
55. Sidgwick, H. *Proc. Soc. psychical Res.* **10**, 25-422 (1894).
56. Finucane, R. C. *Appearances of the Dead* (Prometheus, Buffalo, 1985).
57. Zusne, L. & Jones, W. H. *Anomalistic Psychology* (Erlbaum, Hillsdale, New Jersey, 1982).
58. Edwards, W. in *Formal Representation of Human Judgement* (ed. Kleinmuntz, B.) 17-52 (Wiley, New York, 1968).
59. Nisbett, R. & Ross, L. *Human Inference: Strategies and Shortcomings of Social Judgment* (Prentice-Hall, Englewood Cliffs, 1980).
60. Hoebens, P. H. *Skeptical Inquirer* **1**, 38-45 (1982).
61. Klass, P. J. *Zetetic* **2**, 57-61 (1977).
62. Koestler, A. *The Roots of Coincidence* (Hutchinson, London, 1972).
63. Rhine, L. E. *J. Parapsychol.* **15**, 164-190 (1951).
64. Tart, C. T. *Learning to Use Extrasensory Perception* (University of Chicago Press, 1976).
65. Tart, C. T., Palmer, J. & Redington, D. J. *J. Am. Soc. psychical Res.* **73**, 151-165 (1978).
66. Dixon, N. F. *Preconscious Processing* (Wiley, Chichester, 1981).
67. Fransella, F. & Bannister, D. *A Manual for Repertory Grid Technique* (Academic, London, 1977).
68. Windholz, G. & Diamant, L. *Bull. psychon. Sci.* **3**, 125-126 (1974).

REVIEW ARTICLE

Heavy-electron metals

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A new class of metals has been found in which the electrons have effective masses orders of magnitude larger than the free-electron mass. Some of these metals are superconducting at low temperatures. This superconductivity seems to be unconventional, with an underlying mechanism different from that in all other known superconductors.

AMONG the main developments in physics since the 1930s have been the discovery and exploration of new ground states of condensed matter. Each of these discoveries opened a new chapter in the physics of condensed matter; recent examples are spin- and charge-density waves in metals, the superfluid state of liquid ^{3}He and the quantized Hall effect. Very recently an exciting new class of metallic materials has been discovered with remarkable properties and showing signs of further new ground states. (A general compilation of data, with references current as of mid-1984, can be found in ref. 1.)

The terms 'heavy-electron metal' and 'heavy-fermion system' have been introduced to describe materials in which the electronic states have a characteristic energy orders of magnitude smaller than in ordinary metals. If we write the energy $\varepsilon(k)$ in a free-electron form ($\varepsilon(k) = \hbar^2 k^2/2m^*$), then since the wavevectors $\mathbf{k}$ of the electron determined by the interatomic spacing are not much different, the effective mass m^* must be orders of magnitude larger than the free-electron value and in some cases m^* is a fair fraction of the proton mass. These materials are intermetallic compounds in which one of the constituents is a rare-earth or actinide atom, with partially filled 4f- or 5f-electron shells. At high temperatures these materials behave as if the f-electrons were localized on their atomic sites, as in conventional rare-earth and actinide compounds, where any itinerant electrons are in states derived from loosely bound atomic s-, p- and d-orbitals. As the conventional materials are cooled, the atomic moments due to the f-electrons order spontaneously, mostly antiferromagnetically, less often ferromagnetically. By contrast, in the heavy-electron systems some of the f-electrons become itinerant at low temperatures and form a metallic state with the characteristics described above.

Recently the exciting discovery was made that in some of these new materials the heavy electrons form a superconducting state at very low temperatures[3,4,6]. Superconductivity in ordinary metals is associated with an instability of itinerant electrons; thus it was surprising that it should also occur where normal-state properties are dominated by nearly localized electrons. Various features of this superconducting state are unusual, leading theorists to speculate that not only is the mechanism driving this superconducting transition unconventional, but also that the configuration of the superconducting state is different from that of an ordinary superconductor. Instead of an interaction between electrons that is mediated by phonons (lattice-vibrational quanta), which leads to an essentially isotropic gap in the spectrum of electronic excitations, it is envisaged that a Coulomb interaction between heavy electrons induces a superconducting state in which the energy gap is strongly anisotropic. If this could be definitely established, it would be the culmination of a long search for this phenomenon.

There is no doubt that a proper understanding of this superconducting state requires a clear understanding of the preceding normal state with its remarkable properties. Early theories of the properties of metals always assumed that, whereas the conduction electrons interact with the ionic lattice forming the solid, they do not interact at all among themselves. Quantum statistics then determine the low-temperature properties of this electron gas, two of which are of particular importance in the context of our discussion. The specific heat of this electron gas c_p varies linearly with temperature as $T \to 0$ K (that is, $c_p = \gamma T$). The low-temperature magnetic susceptibility, χ, is independent of temperature. In this simple theory the ratio

$$\chi/\gamma = 3\,\mu_B^2/\pi^2 k_B^2 \qquad (1)$$

is obviously a universal number. $\mu_B = 9.27 \times 10^{-21}$ erg G^{-1} is the Bohr magneton and $k_B = 1.38 \times 10^{-16}$ erg K^{-1} is the Boltzmann constant. The factor which determines the magnitude of both χ and γ is the density of electronic states per unit energy, $N(E_F)$, at the Fermi energy E_F.(E_F is the energy up to which all possible states of the electron gas are occupied at $T = 0$ K.) Hence $N(E_F)$ varies inversely with the characteristic energy of the electrons, leading $N(E_F)$ to be proportional to m^*. This simple concept is quite adequate to describe the qualitative low-temperature features of simple metals, for which γ is of the order of 1 mJ mol^{-1} K^{-1}, $\chi \simeq 10^{-5}$ e.m.u. mol^{-1} and $T_F = E_F/k_B$, the Fermi temperature, is $\sim 10^4$-10^5 K. The experimental facts quoted in

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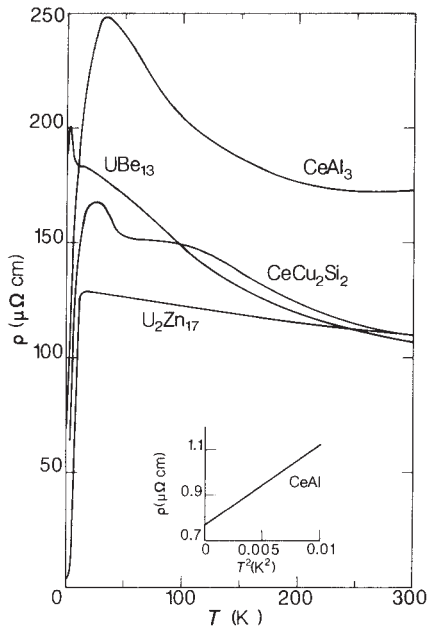

Fig. 1 Temperature dependence of the electrical resistivity ρ of four different heavy-electron compounds below room temperature. The high values indicate very strong scattering of the electrons but the distinct features and the resistivity decrease at low temperatures demonstrate that these are not simply 'dirty' metals. The inset reveals the T^2 dependence of the ρ of $CeAl_3$ at very low temperatures.

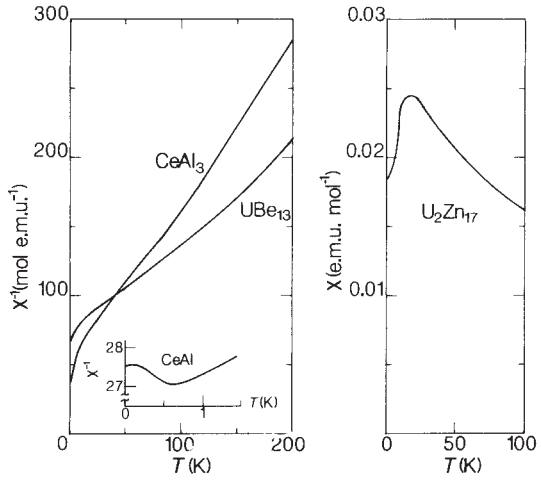

Fig. 2 The Curie–Weiss behaviour of the magnetic susceptibilities χ of $CeAl_3$ and UBe_{13} above 100 K is evidence for localized f-electron moments. The low-temperature saturation (inset) for $CeAl_3$, however, demonstrates the itineracy of the f-electrons below 1.5 K. For U_2Zn_{17}, the tendency to saturation is interrupted by a sharp drop of χ due to antiferromagnetic ordering.

the next section should not only make it clear that these parameters are very different in this new class of materials but also demonstrate the intriguing transition from localized to itinerant behaviour of these heavy electrons.

Normal-state properties

First we consider the electrical resistivity ρ. In ordinary metals ρ decreases rapidly with decreasing temperature below 300 K, from values that are ~1–10 μΩ cm. In heavy-electron materials $\rho \simeq 100$ μΩ cm at room temperature. It often increases with decreasing temperature and only after passing over a maximum at $T \leqslant 50$ K does ρ decrease to low values as $T \to 0$ K. Figure 1 shows examples of this behaviour in $CeAl_3$, $CeCu_2Si_2$, UBe_{13} and U_2Zn_{17}. $CeAl_3$ was the first to be identified as a heavy-electron metal[2]. It stays normal to the lowest temperature investigated ($\sim 10^{-2}$ K) and therefore can be used to study the heavy electrons in their normal state. For $CeAl_3$ it is found that although ρ reaches a maximum value of the order of 200 μΩ cm at 35 K, it drops to less than 1 μΩ cm at $T = 0$ K, where this residual value of the resistivity is determined by impurities and imperfections of the crystal lattice as in ordinary metals. As an intriguing fact it was noted that $\rho \propto T^2$ at the lowest temperatues with a remarkably large pre-factor of 35 μΩ cm K^{-2}, indicating a very effective, temperature-dependent scattering mechanism even at these very low temperatures. (See inset, Fig. 1.)

The first observation of superconductivity in heavy-electron metals was made in $CeCu_2Si_2$ (ref. 3), and this was quite unexpected. As shown in Fig. 1, its $\rho(T)$ is very anomalous in the normal state. The increase of ρ seems to saturate below 100 K but reaches a pronounced maximum in the vicinity of 10 K before it decreases rapidly and finally vanishes discontinuously at the superconducting transition around 0.5 K. UBe_{13} is a 5f-electron-based heavy-electron system, and is also becomes superconducting below 1 K (ref. 4). Its $\rho(T)$ is indeed very much like that of $CeCu_2Si_2$, but the characteristic structures (shoulder and peak) are shifted to lower temperatures. The decrease of ρ below 2.5 K is interrupted by the superconducting transition at 0.9 K, Finally we consider the $\rho(T)$ of U_2Zn_{17}, a substance that orders magnetically from a heavy-electron state[5]. Here the maximum resistivity is observed at 17 K and the rapid decrease of almost two orders of magnitude occurs below 10 K.

Magnetic moments that are due to partially filled 5f-electron shells of individual atoms give rise to the familiar Curie–Weiss-type behaviour of the magnetic susceptibility χ with varying temperature; that is, $\chi^{-1} \propto (T - \theta_p)$ where θ_p is the paramagnetic Curie–Weiss temperature. This type of behaviour is clearly reflected in the plots of χ^{-1} versus T for $CeAl_3$ and UBe_{13} in Fig. 2. Deviations from this simple behaviour are apparent at $T < 100$ K but they can still be ascribed to local f-electron configurations. In both materials χ saturates only at $T \leqslant 1.5$ K (see inset, Fig. 2). In UBe_{13}, χ jumps discontinuously to the ideal diamagnetic value of $(4\pi)^{-1}$ at the superconducting transition (at $T_c \sim 0.9$ K). For U_2Zn_{17}, we show $\chi(T)$ below 100 K; note the trend to saturation and the broad maximum at 17 K. The sharp decrease just below 10 K is due to an antiferromagnetic phase transition. The saturation values of χ for all three materials are very large compared with those of normal metals (3.6×10^{-2} emu mol^{-1} $CeAl_3$; 1.5×10^{-2} emu mol^{-1} UBe_{13}; 2.45×10^{-2} emu mol^{-1} U_2Zn_{17}).

As mentioned above, the electronic specific heat of ordinary metals can be described by a single term, $c_p^{el} = \gamma T$ at temperatures below 10 K. That this is not the case for heavy-electron materials is shown in Fig. 3, where we plot c_p/T against T for $CeAl_3$, $CeCu_2Si_2$ and UBe_{13} for temperatures between 1 and 10 K (Fig. 3*a*) and for UPt_3 (ref. 6) between 1 and 17 K (Fig. 3*b*). For ordinary metals, such a plot would result in a straight line with a positive slope and an ordinate $\simeq 1$ mJ mol^{-1} K^{-2} at $T = 0$ K. For heavy-electron materials in general, the ratio c_p/T rises considerably with decreasing temperature in this temperature range, starting from values of about 100 mJ mol^{-1} K^{-2}. The temperature dependence itself might be loosely interpreted by stating that the γ parameter is no longer constant but is strongly temperature-dependent. Below 1 K, the c_p/T of $CeAl_3$ rises to a maximum of more than 2 J mol^{-1} K^{-2} at about 0.5 K and finally saturates at ~1.6 J mol^{-1} K^{-2} as T approaches 0 K. For both $CeCu_2Si_2$ and UBe_{13}, c_p/T rises in a very similar way but then saturates around 1 K and remains almost constant until a specific-heat anomaly indicates the transition to the superconducting state, as is shown , for example, for UBe_{13} in Fig. 3*c*.

As outlined in the introduction, these very large values of the c_p^{el}/T ratio (or γ value) as T approaches 0 K must be

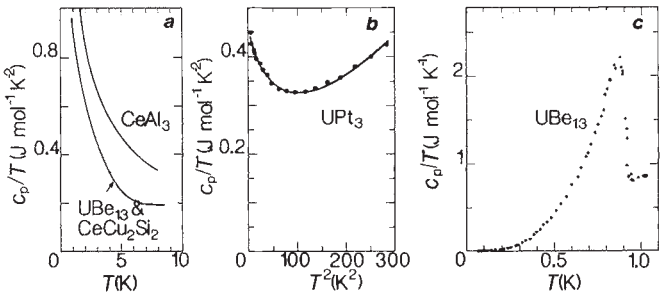

Fig. 3 The low-temperature specific heat c_p of these materials is unusually large. The values of $T \simeq 1$ K are more than a hundred times larger than for ordinary metals and originate in the strong interactions between electrons. An analytic form describing the experimental data has been found only for UPt_3; this is indicated by the solid line in *b*. The specific-heat anomaly of UBe_{13} (*c*) below 1 K is due to the transition to the superconducting state.

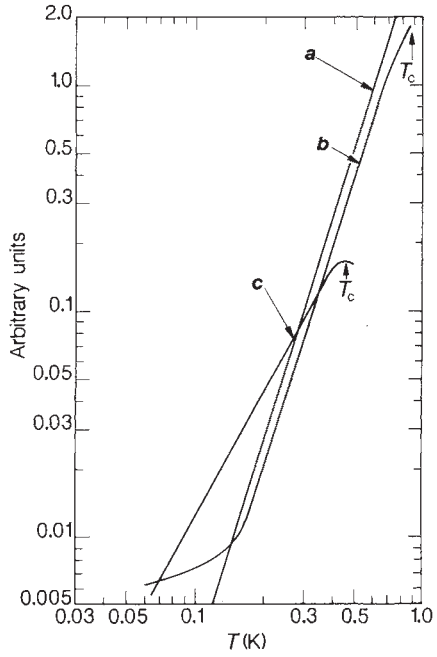

Fig. 4 Examples of the power-law-type temperature dependence of various properties in the superconducting state of UBe_{13} and UPt_3, indicating anisotropic gaps in the electronic excitation spectrum. Conventional isotropic superconductivity would result in exponential temperature dependences for all these physical quantitites. *a*, Specific heat of UBe_{13} ($\propto T^3$); *b*, inverse spin-lattice relaxation rate of ^{9}Be in UBe_{13} ($\propto T^3$); *c*, ultrasonic attenuation in UPt_3 ($\propto T^2$).

interpreted as evidence for enormous densities of states at E_F in the electronic spectrum of these substances. This in turn implies very large effective masses for these electrons, and hence provides the name now generally used for these systems. Although both γ and χ are enhanced in these materials above the values seen in ordinary metals, their ratio χ/γ is comparable to that defined in equation (1).

Phase transitions within heavy-electron state

Superconductivity. The discovery of superconductivity in $CeCu_2Si_2$ by Steglich *et al.*[3] was surprising because it violated many long-held beliefs in the field. In particular, the Curie–Weiss-type high-temperature magnetic susceptibility suggested local magnetic moments on the Ce atoms, and these are known to depress conventional s-state (or singlet) superconductivity by breaking up the Cooper electron pairs.

The specific-heat anomaly (shown for UBe_{13} in Fig. 3*c*) at the superconducting transition temperature (critical temperature, T_c scales with the normal-state value, giving not only convincing proof of bulk superconductivity but also hard evidence that $\gamma(=c_p/T)$ is really due to a large density of states of itinerant electrons. The superconducting energy gap opens in the large-mass band; the f-electrons are therefore intimately involved in the superconductivity. It is important to distinguish this behaviour from that of the Chevrel-phase and ternary-boride magnetic superconductors[7]. In these latter we have an independent sublattice of magnetic ions, the magnetic order parameter of which competes with the superconducting order parameter of the essentially separate conduction electron system; in the heavy-electron materials it is one and the same set of electrons which deliberates between superconductivity and magnetism.

Arguments given below suggest the possibility that the superconductivity observed in these materials may not be of the s-state, isotropic type usual in the Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity[8]. It may instead be an anisotropic p-, or possibly d-state type also possible in a generalized BCS theory, and now quite firmly established as the pairing state in superfluid ^{3}He (ref. 9) but previously unknown in metals. Anisotropic superconducting states may have zeroes of the superconducting energy gap on the Fermi surface and these lead to non-exponential temperature dependences below T_c in experimental measurements such as specific heat, ultrasonic attentuation, thermal conductivity and NMR relaxation rates.

The experimental situation can be illustrated with data for UBe_{13} and UPt_3. In UBe_{13}, the superconducting specific-heat jump at T_c (see Fig. 3*c*) is ~50% larger than the weak-coupling BCS prediction, placing it very squarely in the strong-coupling regime. Below T_c, the specific heat varies with a power law close to T^3 (ref. 10). Ultrasonic attentuation[11] and NMR relaxation rates[12] also follow power laws, as shown in Fig. 4. Deviations from exponential behaviour are found in conventional superconductors containing many magnetic impurities, but the behaviour of the heavy-electron superconductors cannot be explained in this way. In addition, ultrasonic attenuation experiments on UBe_{13} (ref. 13) reveal a peak in attenuation just below T_c, a feature not observed previously in any other superconductor, again suggesting an unconventional form of superconductivity.

The effect of substitutional impurities on the T_c of superconductors is often informative, because impurities carrying local magnetic moments depress T_c in conventional superconductors in a way which varies from impurity to impurity in a predictable way. Local moments are, as mentioned above, strongly pair-breaking for s-state superconductors. In UBe_{13}, the substitution for U of rare-earth impurities with local moments leads to fairly rapid depressions of T_c, but there is no observable difference between those rare-earths which carry local moments and those which do not. Lutetium, for example, at a concentration of 3 atom per cent (at. %) in UBe_{13} has pushed T_c to below 20 mK.

Thorium substitution for U is quite peculiar (Fig. 5). Instead of a monotonic depression of T_c as observed for the rare-earth substitutions in UBe_{13}, an initial depression is followed by a plateau or even a slight rise in T_c at 0.6 K between 2 and 4 at.% Th, after which T_c again decreases, the specific-heat jump being sizeably reduced by the time the Th concentration reaches 6 at.%. Completely unexpected was the finding that there are actually two consecutive second-order phase transitions of comparable magnitude in the plateau region, the lower-temperature one being at approximately 0.4 K (ref. 15). Experiment shows that these samples remain superconducting below the second transition.

This second transition involves an ultrasonic-attenuation anomaly that is two orders of magnitude larger than the first, superconducting one[16]. The similarity to anomalies observed by this technique at magnetic transitions led these authors to suggest that it might be a spin-density-wave transition. The ordered

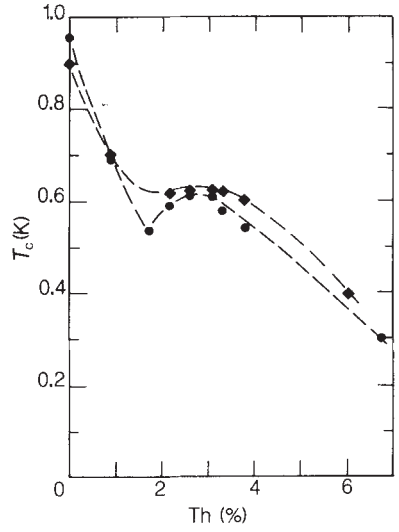

Fig. 5 Influence of small amounts of Th substitution for U in UBe_{13} (ref. 15). Non-magnetic impurities in superconductors usually lead to smooth depressions of the critical temperature T_c. For $0.02 < x_{Th} < 0.04$, a second phase transition occurs at about 0.4 K. Its nature is still not well established. ●, T_c, obtained from magnetic susceptibility; ◆, T_c, obtained from specific heat.

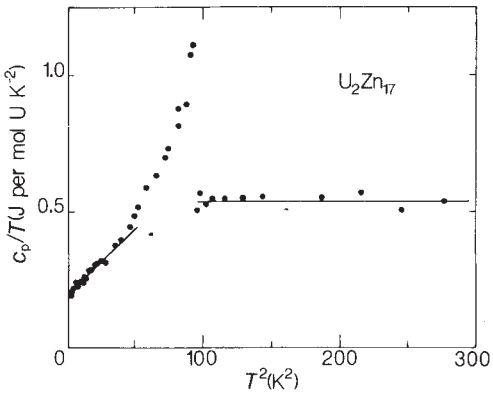

Fig. 6 Electronic specific heat of U_2Zn_{17} at low temperatures. The anomaly is due to the antiferromagnetic ordering. The finite ordinate at T = 0 K indicates that 40% of the large electronic density of states is unaffected by the transition.

magnetic moment would be ~0.01 μ_B/U, consistent with the upper limit set by both NMR and neutron scattering experiments. However, there appears to be no theory at present which can explain how a spin-density wave and superconductivity could co-exist in the same large-mass band.

Another possibility is that the second phase transition is to a second superconducting state. This certainly would require some kind of unconventional superconductivity. The remaining possiblity of a simple structural phase transition is unlikely because, by experience, impurities tend to suppress, not enhance, such transitions.

Magnetism. We illustrate the occurrence of magnetic order in heavy-electron metals with the example of U_2Zn_{17}. It orders at a transition temperature $T_N = 9.8$ K into a simple antiferromagnetic structure with an ordered moment of approximately 0.8 μ_B (ref. 17). This value is considerably smaller than the Curie–Weiss effective moment of 3.3 μ_B. Just above T_N, $\gamma = 504$ mJ per mol UK^{-2}, falling to a limiting value of 198 mJ per mol U K^{-2} as $T \to 0$ K as shown in Fig. 6.

The specific-heat anomaly at T_N shows that the magnetism involves the heavy electrons. Also note that the residual γ is still very large, indicating that some heavy electrons survive in the magnetically ordered state. The magnetic transition can be thought of as removing 60% of the Fermi surface, and this seems to be a general feature of the other known magnetically ordering heavy-electron systems. These systems resemble itinerant-electron magnets such as chromium, not local-moment magnets. This resemblance is strengthened by the fact that the magnetic order in U_2Zn_{17} is strongly affected by substitution on the Zn sites, completely unlike usual local-moment behaviour and very reminiscent of what is observed in Cr.

Theoretical understanding

The fascinating and unusual properties of the heavy-electron metals have attracted the attention of many theorists. Their work can be divided into two broad categories: first, attempts to construct a microscopic theory of the normal-state properties, and second, the use of phenomenological models to examine the experimental consequences of, and the tests for, unconventional superconductivity. Several summaries of current theories have recently been published[18–20].

Normal state. The starting point for the microscopic theories is a periodic version of the model hamiltonian introduced many years ago by P. W. Anderson[21], which serves to describe a single rare-earth or actinide impurity in a conventional metal. There are three parts to this model. One part describes the conduction-electron states derived from s- and p-states as free-electron states and all effects of the Coulomb interaction among these electrons are ignored. In the second part the f-atomic states are described as a set of degenerate energy levels, but because these f-states are spatially localized in the vicinity of the atomic core, the Coulomb interaction between electrons in these states is large and must be included. Consider what will happen if the energy of the degenerate set of f-levels is considerably below the Fermi energy E_F, but the strong Coulomb interaction prevents the f-states from being completely filled. There are now several ground states of the system, because the partially filled f-level can have more than one configuration. The third and complicating part of the Anderson model is the term which describes so-called hybridization, or electron transfer between the f-states and the conduction states. This hybridization is in general a small term, but it allows the possibility of making transitions within this degenerate (in energy) set of ground states so that one particular combination becomes the true ground state. This process has been extensively studied for the single-site impurity case, where it is known as the Kondo effect, after J. Kondo, who posed the problem more than twenty years ago[22]. After many years of theoretical work, exact analytic solutions for this case have been obtained. The solution is characterized by a non-degenerate ground state in which the magnetic susceptibility χ is finite and the entropy associated with the partially filled f-states vanishes linearly in temperature so that the excess specific heat (associated with the impurity) is $\sim \gamma T$. The ratio χ/γ can be enhanced by up to a factor of 2 from the universal form in equation (1). The mixing between the conduction states and the f-states leads to a very large electrical resistance in the limit as $T \to 0$ K.

In the heavy-electron metals the f-state atoms sit on periodic lattice sites and the problem is no longer exactly soluble. Some authors (see refs 18–20) have suggested simply applying what is known about the single-site impurity problem by considering a set of single-site impurities on the lattice. The lattice problem differs from the single-site problem in that coherent states (in solid-state physics terms, Bloch states) can be formed. In other words, the electrons can coherently propagate through the lattice in the same way that wave propagation is possible through coherent diffraction in any periodic set of scatterers. This picture has many attractive features. The coherence of the electronic state causes the resistivity to vanish, thus explaining the low residual resistivity quoted earlier. Secondly the energy scale on

which this coherence occurs would be the single-site Kondo energy, which is determined by the weak hybridization process and is therefore small (typically 10–100 K). Because all the entropy associated with the degeneracies of the f-electron configurations is on the scale of the small Kondo energy, the coefficient γ is much larger than usual and can reach the desired value of $\sim 1\ \mathrm{J\ mol^{-1}\ K^{-2}}$. The magnetic susceptibility is correspondingly large because the opposition to the development of a magnetic moment in the ground state has as its characteristic energy the small Kondo energy.

There are, however, objections to describing these systems as simple collections of single-site Kondo impurities. The description lacks a clear microscopic derivation, and when one tries such a derivation the interaction effects between the sites do not seem to be negligible. An alternative approach is to consider that the essence of the lattice problem is the formation of the coherent Bloch states and that this comes about through the transfer of f-electrons from site to site. However, such transfer processes are severely inhibited by the strong Coulomb intra-site interaction which forbids extra f-electrons on a site. Therefore the only way to obtain f-electron transfer is to remove some f-electrons from the f-levels and place them in the higher energy states near the Fermi energy. This costs energy but it allows coherent hybridization processes to take place, which gain energy. The balance between these two processes leads to a small number of f-electrons being promoted to the higher energy states and a characteristic energy for the coherent state which has a form similar to the single-site Kondo energy. Again χ and γ are determined by this small coherent energy and are large, but the ratio χ/γ may now be larger than the value given by equation (1). A feature common to all approaches is that the large γ values arise from the entropy associated with the degeneracy of the f-configurations or, in other words, the spin degeneracy of the f-states. Another way of describing this feature is that spin fluctuations of the f-electrons are the dominant electronic excitations responsible for the large values of χ and γ at low temperatures.

There is another possible ground state for the lattice problem, namely a state with integral f-electron atomic configurations and ordered local moments on the f-sites. The energy comparison between such a state and the heavy-electron state is an open theoretical question and until it is solved no theoretical predictions can be made as to which of these intermetallic compounds are the more usual antiferromagnetic metals and which are heavy-electron metals.

Superconductivity. There is one condensed-matter system with strong spin fluctuations and a superfluid state: this is liquid ^{3}He. (Note that ^{3}He atoms have spin-1/2 and are fermions, whereas ^{4}He atoms have spin 0 and are bosons. The ^{3}He ground state is called superfluid rather than superconducting simply because ^{3}He atoms are neutral.) Liquid ^{3}He solidifies at a modest pressure, so that in the liquid state the ^{3}He atoms are almost localized and therefore can flip their spins easily. In ^{3}He the superfluid state is known to be an anisotropic p-state (that is, the Cooper pairs of ^{3}He atoms responsible for the superfluid state are in a relative p-state). It has been shown theoretically that the interactions mediated through spin fluctuations favour p-state superfluiditity[23]. Also a relative p-state means a much reduced overlap between the fermions and so is favoured when there is a very strong short-range repulsion as is the case for ^{3}He atoms. The analogy has been made by many authors on both grounds (that is, strong spin fluctuations and strong short-range repulsion) for the heavy-electron systems. In normal metals there is an attractive interaction, mediated by the exchange of phonons, between electrons in states within a Debye energy, $k_B\theta_D$, of the Fermi energy, where θ_D is the Debye temperature. The repulsive Coulomb interaction is reduced for these states because of the mismatch of the energy scale of the Coulomb energy, which is E_F and $k_B\theta_D$. Typically $k_B\theta_D/E_F \simeq 10^{-2}$, but in the heavy-electron metals $k_B\theta_D \geq E_F$ so there is no mismatch. Nevertheless some authors continue to argue for the dominance of phonon-mediated interactions, and therefore for an isotropic or relative s-state pairing. The microscopic theory of the electron pairing necessary to obtain superconductivity in these systems is as yet only qualitative.

Much effort has been put into obtaining a proper description of p-state superconductivity in these crystalline materials which also have important spin–orbit interactions. By the use of group-theoretical techniques the allowed forms can be correctly specified, and there are many possible states which differ in the detailed form of the energy gap which is associated with the electron pairing. In usual s-state pairing the gap is simply isotropic in **k**-space and the electrons are in a relative spin-singlet state. However the global antisymmetry of fermions requires non-trivial structure for the gap in other pairing states where electrons are in spin-parallel or triplet states. As a result, in many of these states, the energy gap vanishes along specific directions in **k**-space.

Clearly the very-low-energy excitations in superconductors with isotropic gaps will differ from those in superconductors with anisotropic gaps which vanish in certain directions. In the former, properties such as specific heat are exponential as $T \rightarrow 0$ K, whereas in the latter they exhibit power-law behaviour (as shown in Fig. 4) as $T \rightarrow 0$ K. The observation of such power-law behaviour, as discussed above (Fig. 4), is taken by many as evidence for anisotropic superconductivity. Unfortunately we lack a decisive way to determine the detailed symmetry of the superconducting state: the equivalent of X-ray and neutron scattering for lattice and magnetic transitions does not exist here. Therefore we must proceed by inference, which can lead, and indeed has led, to differing interpretations.

Conclusions

It is clear from the above that the heavy-electron metals represent an exciting new class of materials. They do not fit into the traditional classifications of materials with partially filled atomic shells; namely, metals, semiconductors or Mott insulators. At high temperatures they are essentially indistinguishable from a host of other rare-earth or actinide intermetallic compounds with local moments arising from the partially filled f-shells. But as the temperature is lowered, instead of forming magnetically ordered structures as is usually the case, these materials unexpectedly form an itinerant or delocalized metallic state. The electrons in this state have a much compressed energy scale and correspondingly high effective mass. The theoretical understanding of how such a state arises out of the f-electrons with their strong Coulomb interactions is today a very active problem and will undoubtedly lead to new insights into the general many-body problem. In particular we would like to know what the material parameters are which determine whether, and under what conditions, a material exhibits this heavy-electron state; we would also like to understand the nature of the residual interactions which characterize this metallic state. It is clear from the discussion above that the heavy-electron metallic state can display the phase transitions seen in many other traditional metals; namely, superconductivity (as in UBe_{13}) and weak (or itinerant) magnetism (as in U_2Zn_{17}). But, as we have stressed, there are many intriguing signs that the superconductivity is not simply the usual isotropic (or s-state) kind. As we have also stressed, this anisotropic superconductivity is expected theoretically when the mechanism responsible for the superconductivity is not the usual electron–phonon interaction. Thus it appears that at last such superconductivity has been found in metals. The confirmation of a second mechanism for superconductivity will spur the search for yet other mechanisms. One of the motivations in this long search was the hope that by achieving superconductivity through unconventional mechanisms, new and possibly higher energy scales would apply, leading to higher values of T_c. This has not yet been obtained, but two important areas must continue to be explored. Materials scientists must

continue the search for a higher T_c, while theorists strive for an improved understanding of the factors which determine and limit T_c. Even modest rises in T_c in these materials might have important technical consequences in the generation of very high magnetic fields, as their superconducting state is extremely stable with respect to magnetic field intensity.

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1. Stewart, G. R. *Rev. mod. Phys.* **56,** 755–787 (1984).
2. Andres, K., Graebner, J. E. & Ott, H. R. *Phys. Rev. Lett.* **35,** 1779–1782 (1975).
3. Steglich, F. *et al. Phys. Rev. Lett.* **43,** 1892–1896 (1979).
4. Ott, H. R., Rudigier, H., Fisk, Z. & Smith, J. L. *Phys. Rev. Lett.* **50,** 1595–1598 (1983).
5. Ott, H. R., Rudigier, H., Delsing, P. & Fisk, Z. *Phys. Rev. Lett.* **52,** 1551–1554 (1984).
6. Stewart, G. R., Fisk, Z., Willis, J. O. & Smith, J. L. *Phys. Rev. Lett.* **52,** 679–682 (1984).
7. Maple, M. B. & Fischer, Ø. (eds) *Superconductivity in Ternary Compounds II* (Springer, Berlin, 1982).
8. Bardeen, J., Cooper, L. N. & Schrieffer, J. R. *Phys. Rev.* **108,** 1175–1204 (1957).
9. Leggett, A. J. *Rev. mod. Phys.* **47,** 331–414 (1975).
10. Ott, H. R. *et al. Phys. Rev. Lett.* **52,** 1915–1918 (1984).
11. Bishop, D. J. *et al. Phys. Rev. Lett.* **53,** 1009–1011 (1984).
12. MacLaughlin D. E. *et al. Phys. Rev. Lett.* **53,** 1833–1836 (1984).
13. Golding, B. *et al. Phys. Rev. Lett.* **55,** 2479–2482 (1985).
14. Maple, M. B. *et al. Phys. Rev. Lett.* **54,** 477–480 (1985).
15. Ott, H. R., Rudigier, H., Fisk, Z. & Smith, J. L. *Phys. Rev.* **B31,** 1651–1652 (1985).
15. Batlogg, B. *et al. Phys. Rev. Lett.* **55,** 1319–1323 (1985).
17. Cox, D. E. *et al. Phys. Rev. B* (in the press).
18. Varma, C. M. *Comments Solid St. Phys.* **11,** 221–240 (1985).
19. Kasuya, T. & T. Saso (eds) *Theory of Heavy Fermions and Valence Fluctuations* Proc. 8th Taniguchi Symp. (Springer, Berlin, 1985).
20. Lee, P. A., Rice, T. M., Serene, J. W., Sham, L. J. & Wilins, J. W. *Comments Con. Matter Phys.* **12,** 99–130 (1986).
21. Anderson, P. W. *Phys. Rev.* **124,** 41–53 (1961).
22. Tsvelick, A. M. & Wiegmann, P. B. *Adv. Phys.* **32,** 453–713 (1983).
23. Anderson, P. W. & Brinkman, W. F. *Phys. Rev. Lett.* **30,** 1108–1111 (1973).

ARTICLES

Molecular stratigraphy: a new tool for climatic assessment

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Variations in sea-surface temperatures over the past 500,000 years are inferred from the relative abundance behaviour of two organic compounds, C_{37} alkenones over the upper 8 metres of a sediment core from the eastern equatorial Atlantic. This molecular record, ascribed to contributions from prymnesiophyte algae, correlates well with the variations in the $\delta^{18}O$ signal for the calcareous skeletons of certain planktonic foraminifera, thus providing the first demonstration of a new stratigraphical technique, which may be especially valuable where methods based on carbonate $\delta^{18}O$ fail.

THE ubiquitous unicellular marine coccolithophorid *Emiliania huxleyi* (Prymnesiophyceae)[1] contains long-chain (C_{37}–C_{39}) di-, tri- and tetra-unsaturated methyl and ethyl ketones (alkenones)[2–4] whose unsaturation changes with growth temperature in laboratory cultures[5]. These compounds also occur in contemporary bottom sediments[6,7], presumably derived from phytoplankton in the photic zone of the overlying water column[8]. Differences in the alkenone unsaturation of contemporary sediments from two different climatic regimes[9] suggest that this feature might reflect, and thereby provide a measure of, water temperatures in the euphotic zone[10]. Accordingly, the distribution of alkenones in many Quaternary marine sediments from various latitudes of different mean sea-surface temperatures (SST) has been examined. We now report the alkenone unsaturation in a gravity core from the eastern equatorial Atlantic ocean, covering the past million years, and compare this record with that of the $\delta^{18}O$ of planktonic foraminifera, an established indicator of a combination of global ice sheet variations and local SST in the euphotic zone[11,12].

Organic compounds

Improved chromatographic and spectrometric methods for the analysis of complex mixtures have greatly extended the number and variety of organic compounds identified in geological materials[13] and have aided the better understanding of their origins and sedimentary fate[13,14]. Often, such marker compounds in bottom sediments can be directly related to their source organisms[14]; a record that can survive passage through food web processes[8] and, subsequently, consolidation and the effects of diagenesis[15]. Such signals best escape disturbance by post-depositional heterotrophic (notably microbial) activity[16] in areas of high sediment accumulation rates and low geothermal gradient[15], as in the deep sea.

The search for organic compounds that are diagnostic of their biological origins in marine sediments[17] and sediment traps[18] has led to the recognition of specific lipid markers for many different types of organisms, including algae such as dinoflagellates[19,20], bacteria, notably methanogens[21], and terrestrial higher plants, such as conifers[22]. In addition, there is the possibility that their distribution patterns may depend on growth conditions; indeed, aquatic organisms can biosynthetically tailor their lipid composition to match environmental conditions of stress[23]. Specifically, they maintain the fluidity of their membranes by changing the molecular composition of the lipid bilayer, either in chain length or in unsaturation[23]. Laboratory culturing experiments show changes in lipid unsaturation, notably for carboxylic acids[24] and wax esters[25], in response to temperature variations. These observations are likely to reflect the behaviour of phytoplankton populations in the natural environment, which may also be preserved in the underlying sedimentary record.

Long-chain alkenones

The less labile constituents of marine phytoplankton include series of long-chain (n-C_{37} to n-C_{39}) alkenones[2,7] which appear to be restricted to a few species of the class Prymnesiophyceae, notably coccolithophorids[3,4] of the family Gephyrocapsaceae. The unsaturation of such compounds shows a temperature dependence (more at lower temperatures) in laboratory cultur-