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Heavy-Electron Metals: New Highly Correlated States of Matter

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Heavy-electron metals exhibit highly correlated electronic behavior at liquid helium temperatures, with conduction-electron masses some hundred times the free-electron mass. Whether “normal,” antiferromagnetic, or superconducting, their electronic behavior differs drastically from their ordinary metallic counterparts. The physical origin of the large mass and unusual superconducting and magnetic properties is the strong coupling between the conduction electrons and the local f -electron moment fluctuations characteristic of these materials.

THE DISCOVERY AND EXPLORATION OF HIGHLY CORRELATED states of condensed matter in this century have opened new chapters in physics. Recent examples include the superfluidity of ^3He (1) and the quantized Hall effect (2). In this article we review the properties of another set of new states, those found in heavy-electron systems, electrically conducting materials in which the conduction-electron specific heat is typically some 100 times larger than that found in most metals (3). As may be seen in Table 1, at low temperatures these systems either remain “normal,” become antiferromagnetic, or become superconducting (4–17). Each of these highly correlated states displays properties that are dramatically different from their counterparts in ordinary metals.

At room temperatures and above, heavy-electron systems behave as a weakly interacting collection of f -electron moments and conduction electrons with quite ordinary masses; at low temperatures the f -electron moments become strongly coupled to the conduction electrons and to one another, and the conduction-electron effective

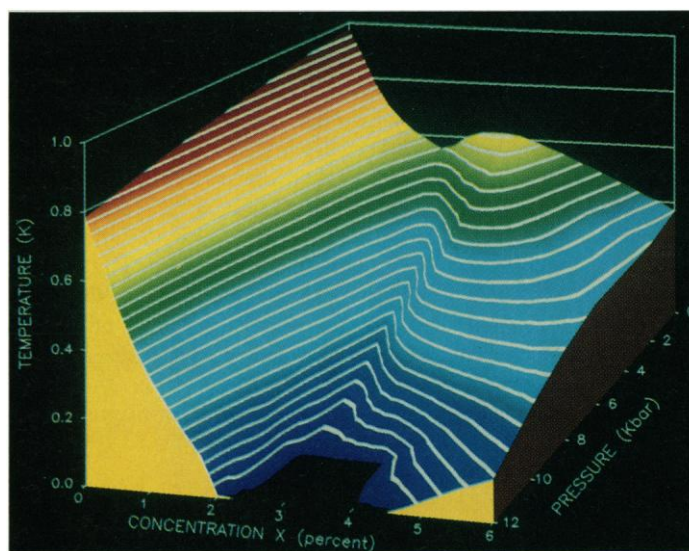


Fig. 1. The superconducting transition temperature (T_c) surface in pressure and concentration (x) space for $\text{Th}_x\text{U}_{1-x}\text{Be}_{13}$.

mass is typically 10 to 100 times the bare electron mass (3). A number of these systems become superconducting, a quite surprising result given the fact that in ordinary superconductors a dilute concentration of magnetic impurities destroys superconductivity (18). Indeed in both UPt_3 (19) and URu_2Si_2 (5) recent experiments suggest that on lowering the temperature an antiferromagnetic transition is followed by a transition to the superconducting state, whereas in $\text{U}_{0.97}\text{Th}_{0.03}\text{Be}_{13}$ the order of the transitions is reversed (9). Moreover, we shall see that the physical mechanism responsible for superconductivity is an attractive interaction between electrons that results from a virtual exchange of local moment fluctuations, rather than the exchange of phonons that leads to superconductivity in ordinary metals.

Thus in heavy-electron systems one sees realized two long-

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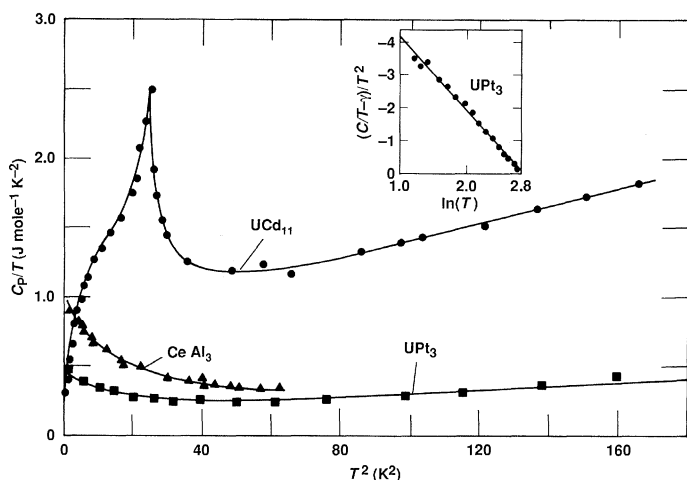


Fig. 2. The specific heat at constant pressure C_p divided by temperature T plotted versus T^2 for UCd_{11} , CeAl_3 , and UPt_3 . The inset shows a fit to $C_p = \gamma T + \beta T^3 + \delta T^3 \ln(T)$ for UPt_3 .

cherished beliefs of the late Bernd Matthias: that superconductivity and magnetism are not mutually inimical, and that a magnetic interaction can give rise to superconductivity. Matthias (20) first put magnetic impurities into superconductors some 30 years ago to explore these possibilities. Although he did not discover heavy-electron superconductors, his seminal investigations and his drive to explore new materials have been a continuing source of inspiration.

Figure 1 illustrates the richness of response of heavy-electron systems to the addition of impurities. There one sees that at zero pressure on adding minute amounts of thorium (a nonmagnetic impurity, which primarily acts to increase the system volume) to UBe_{13} , the transition temperature decreases markedly until, at an impurity concentration of $\sim 2\%$, a cusp in the transition temperature (T_c) curve appears: further additions of thorium lead to an increase in T_c , accompanied by a second transition at $T \sim 0.4$ K (11). Recent muon spin relaxation experiments (9) show that the second transition is accompanied by the onset of magnetism. The application of pressure P (21) to the system shifts the transitions; for $P \geq 9$ kbar, superconductivity is completely absent for a range of concentrations; at 12 kbar that range is between $\sim 2.5\%$ and $\sim 4.5\%$ of thorium. This remarkable phase diagram results from the highly concentration-dependent interplay between antiferromagnetic moment fluctuations and superconductivity.

Normal State Behavior

Some unique features of the low-temperature normal state properties of heavy-electron systems [Fig. 2 and Table 2; see (22–39)] include:

1) An anomalously large specific heat. The ratio of specific heat to temperature, $C(T)/T \equiv \gamma(T)$, is a measure of the temperature-dependent electronic density of states near the Fermi surface, and as shown in Table 2, for temperatures below 10 K is some two or more orders of magnitude in excess of that observed in ordinary metals. Moreover, $\gamma(T)$ continues to be highly temperature-dependent for temperatures below 10 K—a striking contrast to the temperature-independent γ usually observed in a metal (Fig. 2).

2) Highly temperature-dependent de Haas–van Alphen oscillation amplitudes measured at $T \lesssim 0.1$ K in UPt_3 (40) and CeCu_6 (41) that confirm the presence of conduction electrons with effective masses one to two orders of magnitude greater than observed in ordinary metals.

3) A magnetic susceptibility, $\chi(T)$, that continues to vary with

temperature below 20 K, and is some two or more orders of magnitude larger than the temperature-independent Pauli susceptibility observed in this region in an ordinary metal. The susceptibility is highly pressure-dependent, as evidenced by a magnetostriction (42) that exceeds that of a transition metal by two or more orders of magnitude.

4) A usually negative thermal expansion, the magnitude of which dwarfs the positive thermal expansion of an ordinary metal by some four orders of magnitude (43).

5) Low-temperature transport properties that differ markedly from those of ordinary metals. For example, the resistivity displays a rapid variation with temperature below 10 K, whereas the resistivity of a normal metal, dominated by impurity scattering, is nearly constant over this region. For a number of heavy-fermion systems, the low-temperature resistivity takes the form $\rho = \rho_o + \rho_{ee}T^2$ at the lowest temperatures. The temperature-independent contribution, ρ_o is comparable to that found in moderately pure ordinary metals, whereas the coefficient, ρ_{ee} , which measures the importance of electron-electron scattering, is six to nine orders of magnitude larger than its value in an alkali metal.

6) A remarkable sensitivity to impurities. For example, the substitution of 3.4% of the uranium in UBe_{13} by thorium leads to a 37% increase in $\gamma(0)$, whereas the substitution of a similar amount of lutetium depresses γ by the same amount (44).

The following high-temperature ($T \geq 200$ K) properties of heavy-electron systems, summarized in Table 3 (45–52), are also of interest:

1) A magnetic susceptibility of the Curie-Weiss form, $\chi = C/(T - \Theta_{CW})$, where C is a constant. Note that for heavy-electron systems the Curie-Weiss temperature Θ_{CW} is negative, and the effective moment, deduced from C , lies between the value 2.54 Bohr magnetons (μ_B) expected for a free atom with a single f -orbital occupied, and that of $\sim 3.6\mu_B$, obtained for a free atom that respects Hund's rules and has 2 or 3 f -orbitals occupied; the single exception is CeCu_6 (along one crystallographic direction).

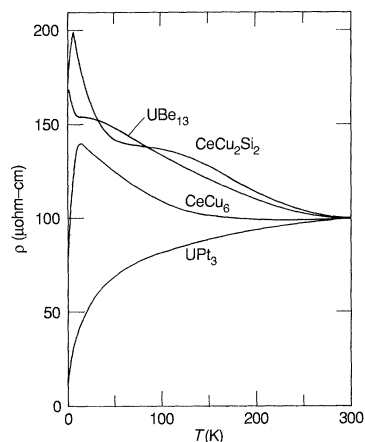
2) A large, nearly temperature-independent resistivity at room temperature, which is some two orders of magnitude larger than that of sodium, and an order of magnitude larger than that of palladium. Moreover, in all heavy-fermion compounds other than UPt_3 and UAl_2 , the resistivity near room temperature increases as the temperature is decreased, whereas in normal metals the opposite behavior is observed.

Table 1. Ordering in some heavy-electron systems. Numbers in parentheses are literature citations.

Ordering temperature (K)	
Antiferromagnetic	
UAgCu_4	18.15 (4)
URu_2Si_2	17.0 (5)
UCu_5	15.2 (4, 6)
U_2Zn_{17}	9.7 (7)
UCd_{11}	5.0 (8)
$\text{U}_{0.97}\text{Th}_{0.03}\text{Be}_{13}$	0.4 (9)
Superconductive	
URu_2Si_2	1.5 (5)
UBe_{13}	0.9 (10)
$\text{U}_{0.97}\text{Th}_{0.03}\text{Be}_{13}$	0.6 (11)
CeCu_2Si_2	0.65 (12)
UPt_3	0.50 (13)
No ordering	
UAuPt_4	0.15* (14)
CeAl_3	0.02* (15)
CeCu_6	0.02* (16)
UAl_2	0.02* (17)

*Lowest temperature at which measurements have been made.

Fig. 3. The resistivity versus temperature for several heavy-electron compounds displaying a range of behaviors. Note that the resistivities at room temperature have been normalized to the same value.



The intermediate temperature regime ($10 \text{ K} \lesssim T \lesssim 300 \text{ K}$) is characterized by unusual structure in thermodynamic and transport properties:

- 1) A peak in the resistivity observed in most heavy-electron systems— UPt_3 and UAl_2 again being the exceptions (Fig. 3).
- 2) In materials that do not order magnetically, a peak in the specific heat at roughly the same temperature as the resistivity maximum.
- 3) A large positive maximum in the Hall coefficient observed in UPt_3 (53), CeAl_3 (53), UAl_2 (53), CeCu_6 (54), and UBe_{13} (54) (Fig. 4). There is no simple correlation between this feature and any structure in the resistivity.

Heavy-Electron Antiferromagnets

Properties characterizing the heavy-electron antiferromagnetic state include:

- 1) A Néel temperature, T_N (see Table 1), typically 10 to 20% of $|\Theta_{\text{CW}}|$.
- 2) A simple arrangement of the ordered moments. The ordered moments are commensurate with the uranium sites. In U_2Zn_{17} , the direction of the moment alternates from uranium site to uranium site (55), but in UCu_5 the moments are aligned ferromagnetically within a plane and antiferromagnetically between planes (56).
- 3) A magnetic moment in the ordered state at most only 40% of the effective moment deduced from the high-temperature susceptibility.

4) A total entropy that is very much less than that one would expect for a collection of disordered moments. Moreover, the total entropy below T_N is approximately 25 to 30% less than $\gamma(T_N)T_N$. This has led to the speculation (57) that were it not for the onset of magnetic ordering, $\gamma(T)$ would continue increasing with decreasing temperature.

5) A T_N that is in general weakly pressure-dependent, the exception being UCd_{11} , which develops two additional phase transitions (at 3 kbar and at 16 kbar) below T_N (58).

6) An unusual sensitivity to impurities. For example, in U_2Zn_{17} , replacement of 2% of the zinc atoms by copper (which has no magnetic moment) totally suppresses the magnetic state, whereas $\gamma(0)$ is increased by some 10% (59).

7) A large linear contribution to the specific heat below T_N . Extrapolations of $\gamma(T)$ to zero temperature from specific heat data obtained in the antiferromagnetic states of U_2Zn_{17} and UCd_{11} give a finite $\gamma(0)$ that is some 40% of that obtained by extrapolating the paramagnetic specific heat data to $T = 0$ (60). This suggests that heavy electrons exist in the antiferromagnetic state. Moreover, for UAgCu_4 and UCu_5 , $\gamma(T)$ increases with decreasing T for $T \lesssim 0.2 T_N$ (4).

Systematics

It is known that cerium and uranium, and in a few cases other f -elements, can form heavy-electron compounds. Although we have little predictive capability concerning the formation of heavy-electron states, certain patterns in their occurrence are clear. Hill (61) first pointed out that when the f - f spacing in cerium and uranium intermetallic compounds is less than approximately $3.4 \text{ \AA}$, f -bands can form, and nonmagnetic behavior results. Magnetic behavior occurs at larger separations. For heavy-electron behavior it appears to be necessary for the f -atoms to be beyond this Hill limit of $3.4 \text{ \AA}$, whereas the absence of f -atom near neighbors seems necessary for very large γ . (UAl_2 , whose $\gamma = 140 \text{ mJ mol}^{-1} \text{ K}^{-2}$, does have uranium-uranium near neighbors.) The magnetic behavior of both cerium and uranium varies strongly with their apparent atomic radii in the compounds; large radii favor local moment behavior and the formation of heavy-electron states.

Another regularity emerges when one examines where elements that form heavy-electron binary compounds with uranium occur in the periodic table. These are found at the end of the d -block and the beginning of the sp -blocks where few states are available for hybridization with the f -electrons. This has led to the suggestion

Table 2. Some low-temperature properties of heavy-electron compounds compared with those of palladium and sodium. All quantities are inferred from measurements at the lowest temperatures for which the normal state has been investigated. Numbers in parentheses are literature citations. Multiple values separated by slashes indicate different crystallographic directions.

Material	$\gamma(0)$ ($\text{mJ mol}^{-1} \text{ K}^{-2}$)	$\gamma(0)$ ($\text{mJ cm}^{-3} \text{ K}^{-2}$)	$\chi(0)$ ($10^{-3} \text{ emu cm}^{-3}$)	ρ_0 ($\mu\text{ohm cm}$)	ρ_{ee} ($\mu\text{ohm cm K}^{-2}$)
CeAl_3	1620 (15)	18.47	0.41 (15)	0.77 (15)	35 (15)
CeCu_6	1300 (16)	20.53	0.28 (22)	18.1/5.71/10.6 (45)	—
CeCu_2Si_2	1000 (12)	20.00	0.13 (23)	4.8 (24)	10.7 (24)
URu_2Si_2	180 (5)	3.66	0.03/0.10 (5)	33 (25)	0.17/0.10 (25)
UAl_2	142 (26)	4.25	0.13 (27)	17 (27)	0.053 (27)
UCu_5	> 250 (4)	4.8	0.18 (28)	—	—
U_2Zn_{17}	500 (7)	5.08	0.19/0.24 (29)	—	—
UCd_{11}	840 (8)	5.21	0.24 (8)	—	—
UPt_3	450 (13)	10.6	0.19/0.10 (30)	0.5 (31)	0.5 (31)
UAuPt_4	725 (14)	10.5	0.22 (14)	—	—
UBe_{13}	1100 (10)	13.5	0.18 (10)	18 (32)	—
Pd	10 (33)	1.12	0.08 (34)	4.28×10^{-4} (35)	6.4×10^{-5} (35)
Na	1.5 (36)	0.063	0.0011 (37)	0.9×10^{-3} (38)	1.0×10^{-6} (39)

(62) that hybridization is hostile to formation of the heavy-electron ground state. It is also clear that elements that form heavy-electron compounds with uranium lie between those that give rise to nonmagnetic uranium-compounds and those that yield well-localized f -moment uranium-compounds. The surprising sensitivity of low-temperature phase transitions of heavy-electron systems to certain small impurity additions can thus be viewed not as a simple dirt effect, but as a delicate function of the valence and volume of the impurity.

The local chemical environment of the f -atom is clearly important. An example (14) of how sensitive the many-body effects can be to this is provided by UPt_5 . This cubic compound has a slightly enhanced γ of $85 \text{ mJ mol}^{-1} \text{ K}^{-2}$. Substitution of platinum by gold to form UAuPt_4 , which has the same crystal structure, changes γ to $700 \text{ mJ mol}^{-1} \text{ K}^{-2}$. It is believed that here uranium is tetrahedrally coordinated by gold.

Although many of the bulk properties of the heavy-electron compounds are extreme, ratios such as γ/χ have values similar to those of simple metals (60). It is instructive to tabulate the heavy-electron compounds with respect to γ_v , the γ per unit volume (see Table 2). The tabulation (60, 62) for the uranium heavy-electron compounds shows a surprising regularity as γ_v increases, from spin fluctuating systems to magnetically ordered heavy-fermion systems to superconducting heavy-fermion systems. It is a task of theory to understand why the superconductors occur at largest γ_v , and why, additionally, these particular heavy-electron compounds seem to have γ/χ closest to the free-electron value.

Physical Picture

We have seen that the physical behavior of heavy-electron systems changes dramatically as the temperature is lowered. Consider the magnetic susceptibility: at high temperatures its temperature dependence is that of a collection of local moments, whose magnitudes are close to those found in free atoms; at low temperatures its large and nearly temperature-independent value is of the same order of magnitude as a metal in which the itinerant electron density of states is two or more orders of magnitude larger than that encountered in normal metals. The fact that in the nonmagnetic normal state at low temperatures, the specific heat has a large contribution, which varies as T in many cases, suggests that itinerant electrons, with an effective mass comparable to the muon mass, dominate the thermal behavior there. In similar fashion, the low-temperature transport properties exhibit the behavior expected (63) for a Fermi liquid made up of heavy electrons that scatter against impurities, against localized spin fluctuations, and against one another.

Thus, at high temperatures, heavy-electron systems behave like a weakly interacting collection of local moments and conduction electrons, whereas at low temperatures, so far as thermal and transport properties are concerned, these systems behave like a collection of heavy itinerant electrons that scatter against one another and may, under some circumstances, exhibit a transition to a superconducting state. Accounting for the transition between these two regimes is a central problem in understanding heavy-electron systems. The transition is not a sharp one (in the sense of ordinary phase transitions) and may be viewed as a transformation or metamorphosis, a reversible analogue of the process in the chrysalis by which a caterpillar becomes a butterfly. In both cases the end product can be simply characterized, whereas the physical behavior evidenced during the transformation is complex and defies simple characterization.

In the course of the transformation, as the temperature decreases, the entropy, S_μ , of the disordered local moments is effectively

Table 3. Some high-temperature properties of heavy-electron compounds compared with those of palladium and sodium. Numbers in parentheses are literature citations. Multiple values separated by slashes indicate different crystallographic directions.

Material	$-\Theta_{\text{CW}}$ (K)	μ_{eff} (μ_B)	ρ ($T = 300 \text{ K}$) ($\mu\text{ohm cm}$)
CeAl ₃	46 (45)	2.63 (45)	65 (15)
CeCu ₆	59/59/8 (16, 46)	2.6/2.67/2.46 (16, 46)	70/70/70 (16, 46)
CeCu ₂ Si ₂	140 (47)	2.68 (47)	90 (48)
URu ₂ Si ₂	65 (5)	3.51 (5)	324/169 (25)
UAl ₂	245 (27)	3.1 (27)	190 (27)
UCu ₅	284 (28)	3.52 (28)	286 (28)
U ₂ Zn ₁₇	105 (29)	3.3 (29)	110 (7)
UCd ₁₁	23 (8)	3.45 (8)	80 (49)
UPt ₃	200 (30)	3.0 (30)	130 (31)
UAuPt ₄	135 (14)	3.21 (14)	135 (14)
UBe ₁₃	53 (10)	3.1 (10)	107 (10)
Pd	86 (50)	4.6 (50)	10 (51)
Na	—	—	5 (52)

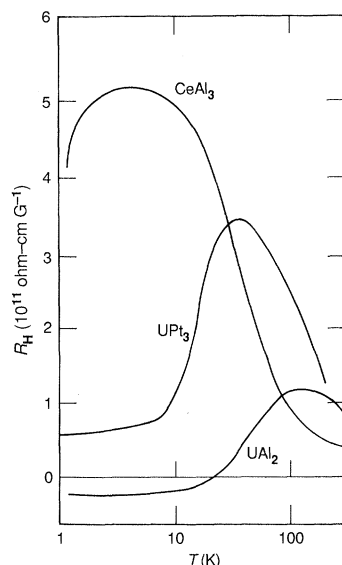
transformed into that of the itinerant electrons. Thus, as might be expected, one has $\gamma \sim (S_\mu/\Theta_{\text{coh}})$, where Θ_{coh} is some measure of the temperature that characterizes the crossover between high and low temperature behavior. A physical picture of this transformation is that as the temperature is lowered, the local moments and conduction electrons become more and more strongly coupled. The magnetic behavior is quenched, whereas the effective mass of the itinerant electrons becomes larger.

Kondo Systems

It is natural to inquire whether there are any other systems that display similar behavior. One class, which is frequently mentioned in connection with heavy-electron systems, is simple metals containing dilute concentrations of magnetic impurities. The physical properties of these systems are successfully described by the Kondo model (64) in which a d - or f -level of the impurity has an energy just below the Fermi level. At high temperatures the impurity displays local-moment behavior, whereas at low temperatures the spin of the impurity is compensated by a conduction electron cloud, and the magnetic susceptibility is independent of temperature and has a higher value than its free-electron value. The increase reflects the existence of a narrow resonance, of width $\sim T_K$, the Kondo temperature, in the scattering of conduction electrons by the impurity spin and its compensating cloud; the increase is of order $x_{\text{imp}} T_F/T_K$, where x_{imp} is the impurity concentration and $k_B T_F$ the conduction-electron Fermi energy. An additional contribution to the magnetic susceptibility, which can be of the same order of magnitude, comes from an induced effective interaction between the conduction electrons, which is produced by a polarization of the compensated impurity spins. A final contribution to the magnetic susceptibility comes from the polarization of the compensated impurity spins by the external magnetic field.

Kondo systems have a finite electrical resistivity as a consequence of the scattering of the conduction electrons by the compensated impurity spin. The resistivity is a maximum at zero temperature, where the scattering is resonant, and it falls off as $(T/T_K)^2$, in part because the scattering is off resonance, and in part because of the importance of inelastic scattering. On the other hand, the specific heat, linear in temperature at low temperatures, reaches a maximum at temperatures $\sim T_K$, beyond which it falls off with increasing temperature. Nozières (65) has constructed a Fermi liquid model for the behavior of the conduction electrons around the impurity, and has shown how the low-temperature behavior of the specific heat,

Fig. 4. Hall coefficients versus temperature for CeAl_3 , UPt_3 , and UAl_2 .



resistivity, and magnetic susceptibility, brought about by the temperature-dependent Kondo resonance, can be expressed in terms of a few Fermi liquid parameters.

At first sight one might hope to explain the properties of heavy-fermion systems by regarding them as a collection of independent compensated spins, with properties similar to those described above, placed on a lattice. [Calculations based on such a model are reviewed in Fulde *et al.* (3).] However, this picture cannot be true in detail. First, in this picture one would expect all heavy-fermion systems to exhibit maxima in the resistivity, a prediction in conflict with experiments. This maximum would come about because scattering from a magnetic site is partly elastic and partly inelastic. When the sites are in a periodic array, only the inelastic scattering leads to real scattering processes, whereas the elastic scattering creates band structure in the electron spectrum. The total cross section for a single magnetic site to scatter an electron increases as the temperature decreases, and the scattering becomes increasingly elastic at temperatures below the Kondo temperature. At high temperatures the significant scattering is inelastic, whereas at $T = 0$ it is completely elastic. Consequently, as the temperature decreases, the inelastic scattering cross section first increases, reflecting the increase in the total cross section, and then decreases to zero at $T = 0$.

Second, with a finite density of magnetic impurity sites, the interaction between the itinerant electrons is no longer determined by the polarization of a single compensated impurity spin, but rather reflects the presence of other compensated spins, whereas the repeated interaction of the itinerant electron-hole pairs can both screen the effective interaction between compensated spins, and give rise, at low temperatures, to markedly enhanced low-frequency spin fluctuation excitations.

Third, in the Kondo model, the susceptibility at high temperatures displays Curie-Weiss behavior, where as a result of the partial compensation of local moments by conduction electrons, Θ_{CW} is $\sim T_K$. Since, however, in heavy-electron systems the moments interact with one another by way of their coupling to conduction electrons, there will also be the usual Weiss molecular field contribution to Θ_{CW} , proportional to the strength, J , of the induced interaction between moments.

We have assumed that the f -electrons are confined to the magnetic sites, but in reality they can hop into the conduction band, as in the Anderson model (66). [For a review of theoretical calculations based on the periodic-Anderson model, see Fulde *et al.* (3).] As a consequence of this, the itinerant heavy-electron states at low

temperatures are superpositions of localized electrons and conduction electrons. Their quite strong interaction reflects not so much their direct Coulomb interaction, as it does an interaction induced by their coupling to spin fluctuations on the magnetic sites, and it provides a natural explanation for the large finite-temperature corrections to the low-temperature form of the specific heat, and the strong temperature dependence of the electrical resistivity and other transport coefficients.

Fermi Liquid Theory

In the low-temperature limit the thermal and transport properties of heavy-fermion systems in the normal state should be those expected for heavy-electron Fermi liquids. However, in most cases experiments have not yet been carried out in the Landau limit, that is, at temperatures sufficiently low that one can neglect, in first approximation, the frequency dependence of the quasiparticle energies and quasiparticle scattering amplitudes associated with the coupling of the conduction electrons to the localized f -electrons. If we define Θ_{coh} as the temperature below which the electronic specific heat is linear in T , and the electrical and thermal resistivities fall off sharply with decreasing temperature, then it is only at temperatures $T \ll \Theta_{\text{coh}}$ that one expects to observe the Landau temperature dependence, in which the finite temperature corrections to the low-temperature limiting behavior of the electrical resistivity, ρ (Fig. 5), the thermal resistivity times the temperature, WT , and the ultrasonic attenuation coefficient α (Fig. 6) are proportional to T^2 . Such Landau limiting behavior is observed for UPt_3 at temperatures below ~ 1.5 K (31), but UBe_{13} at zero pressure becomes a superconductor well before it reaches a temperature at which Landau theory would apply (63, 67).

Landau theory is a very general framework that makes few specific assumptions about the nature of the system to be described; detailed microscopic physics is contained in the parameters that enter the theory (68). It has proved to be highly successful in providing an account of the low-temperature properties of the "canonical" Fermi liquid, ^3He (69). Quite generally, it predicts a low-temperature specific heat containing the well-known term linear in T . Interactions between quasiparticles lead to $T^3 \ln(T)$ contributions to the specific heat as well as a quasiparticle collision rate proportional to T^2 . In ^3He the most important contribution to the quasiparticle scattering amplitude is the exchange of spin fluctuation excitations,

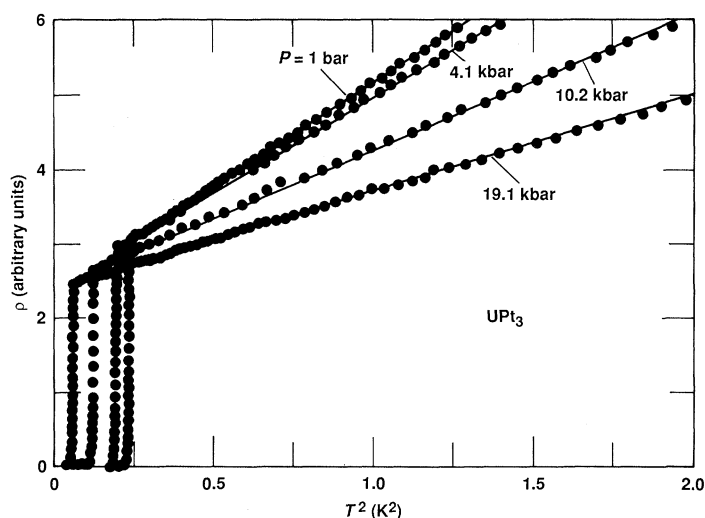
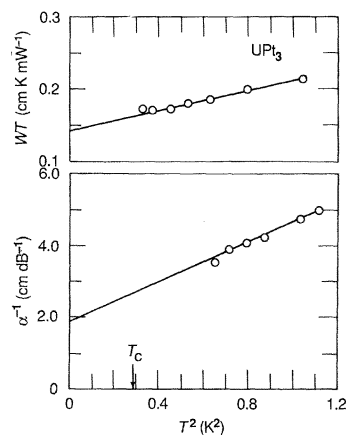


Fig. 5. Resistivity versus temperature squared for UPt_3 at the pressures indicated.

Fig. 6. (Top) The thermal resistivity W times temperature T and **(bottom)** the inverse of the ultrasonic attenuation coefficient α^{-1} versus temperature squared for UPt_3 . The superconducting transition is indicated by the arrow.



and it is this interaction that is responsible for the large $T^3 \ln(T)$ contribution to the specific heat, and for the transition to the superfluid state. The appearance in UPt_3 of a large $T^3 \ln(T)$ term in the specific heat and superconductivity led Stewart *et al.* (13) to suggest that spin fluctuations might play a role in this heavy-fermion compound comparable to that in ^3He .

At first sight one might hope to be able to make quantitative calculations for heavy-electron systems by straightforward application of Landau theory. However, there are significant differences between heavy-fermion systems and ^3He that make Landau theory for heavy-fermion systems much more complicated than for ^3He . As a result of the crystal lattice, heavy-fermion systems are intrinsically anisotropic and the electrons are not Galilean invariant. One consequence of the latter effect is that the electron effective mass is not simply related to a moment of the quasiparticle interaction. Because of spin-orbit coupling, the nature of the quasiparticle states is difficult to specify and their magnetic moments are not simply related to the free-electron moment, and, more important, there are significant nonquasiparticle contributions to the static magnetic susceptibility, so that quasiparticle properties cannot be deduced directly from measurements of the susceptibility.

An initial attempt at applying Fermi liquid theory to UPt_3 has been made by Pethick *et al.* (70) and by Hess (71). They have approximated UPt_3 as an isotropic Fermi liquid of pseudo-spin $1/2$ particles and have shown that it is possible to obtain a quantitative account of the compound's low-temperature thermal and transport properties, and of the quasiparticle contribution to the spin fluctuation excitation spectrum, starting with a single Fermi liquid parameter [for a review of this approach, see (63)]. The recent de Haas-van Alphen measurements of Taillefer *et al.* (40) show that the Fermi surface is multisheeted, consistent with density-functional calculations. The Fermi surface, therefore, is more complicated than assumed in the earlier calculations and is characterized by considerably smaller values of Fermi wave number k_F and effective mass m^* . Consequently, the agreement with experiment may prove to be fortuitous.

Magnetic Properties

We turn now to a consideration of the magnetic properties of heavy electrons. Here one needs to take into account explicitly the presence of compensated local moments at each lattice site. We recall that the same strong coupling between the f -electrons and the conduction electrons, which is responsible for the heavy itinerant quasiparticles, will give rise to a compensating electron cloud that will alter the magnetic response of the local moments. If magnetiza-

tion were a conserved quantity, the local moments and their compensating electron clouds would not contribute to the long wavelength magnetic susceptibility, $\chi(T)$, at low temperatures; that quantity would be entirely determined by the heavy-electron quasiparticle contribution, χ_{qp} . Because magnetization is not conserved, there can be a significant nonquasiparticle contribution, χ_{loc} to $\chi(T)$, which arises from the polarization of the local moments and their compensating clouds (that is, from virtual excitations at finite frequencies). This polarization, in the Kondo model, would correspond to finite-energy transitions between the singlet ground state and finite spin excited states.

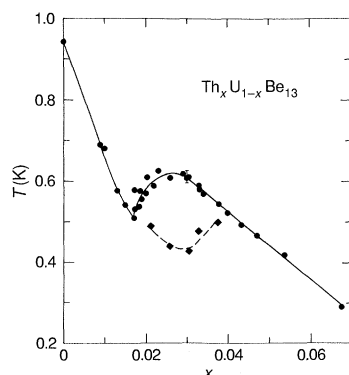
In neutron scattering experiments, which measure the spin fluctuation excitation spectrum, one would therefore expect to see long wavelength excitations of two sorts: (i) those associated with itinerant heavy electron-hole pairs, whose frequency vanishes in the long wavelength limit, and (ii) those from the compensated moments of the f -electrons at magnetic sites, whose frequency remains finite in the long wavelength limit. The present evidence is that in the four heavy-electron systems for which detailed neutron scattering experiments have been carried out [UPt_3 (72), U_2Zn_{17} (73), URu_2Si_2 (74), and CeCu_6 (75)], the dominant contributions to the measured spin fluctuation excitation spectra are those of the compensated local moments. Evidence for antiferromagnetic coupling between local moments on different sites is found for all these systems. As was the case at high temperatures, this interaction reflects not a direct exchange, but rather one induced by the coupling of the local moments to the itinerant electrons. A model in which that interaction is constant between nearest neighbors has been shown (75) to provide a fit to the data in CeCu_6 , whereas for U_2Zn_{17} a temperature-dependent nearest neighbor interaction that increases with decreasing temperature below 18 K has been found (73) to drive the antiferromagnetic transition at 9.7 K.

The presence of heavy itinerant electrons in the antiferromagnetic state is consistent with the above picture, since it is the local moments that order antiferromagnetically as a result of nearest neighbor coupling. The observed reduced state density could result from either a change in the area of the Fermi surface occupied by the heavy electrons, or may reflect a change in the average Fermi velocity v_F of these electrons. To the extent that the physical origin of the antiferromagnetic behavior is the local moment interaction, it is likely that nesting of the Fermi surface plays little role; hence it would seem plausible that the Fermi surface area occupied by the heavy electrons is relatively unchanged, and what is observed is a substantial increase of their average Fermi velocity. A change in v_F should not be surprising, since it is the coupling between the itinerant electrons and the local moments that is responsible for the heavy-electron mass, and this coupling will change below T_N , since there the spectrum of local moment fluctuations will change, as a consequence of the appearance of antiferromagnetic spin waves characteristic of the ordered magnetic state.

The compound URu_2Si_2 is a particularly interesting system because it exhibits both an antiferromagnetic transition at 17.5 K and a subsequent superconducting transition at $T_c \approx 1.2$ K (5). In this system the attractive interaction between the heavy itinerant electrons induced by their coupling to the antiferromagnetic spin waves would seem a strong candidate for the physical origin of the superconducting transition.

In UPt_3 , one can show (72) from the neutron scattering results for χ_{loc} that the magnitude of the local fluctuating magnetic moment is considerably less than its high-temperature value, whereas the quasiparticle effective magnetic moment is markedly reduced below a Bohr magneton. Neither of these reductions should be regarded as especially surprising, given the antiferromagnetic nature of the correlations that characterize heavy-electron behavior.

Fig. 7. Phase diagram of $\text{Th}_x\text{U}_{1-x}\text{Be}_{13}$ displaying the onset of superconductivity and, over a restricted range of x , of a second transition. Circles are ac susceptibility and diamonds are specific heat.



Superconductivity

To put in perspective the ways in which heavy-fermion superconductivity differs from that of ordinary metals, we review the salient features of the successful microscopic theory of superconductivity developed by Bardeen, Cooper, and Schrieffer (BCS) (76). The attractive interaction between electrons that is brought about by exchange of virtual phonons gives rise to an instability in the behavior of pairs of electrons near the Fermi surface in singlet states, and leads to a gap in the electron spectrum at the Fermi surface. This gap is finite everywhere on the Fermi surface, and as a consequence many properties, such as the specific heat and transport coefficients, fall off exponentially with decreasing temperature. The orbital part of the wave function associated with the pairs has *s*-like character, and the gap is essentially constant over the Fermi surface. In some metals the crystal lattice can introduce some anisotropy in the gap, but in most cases this is modest.

In the decade or so following the development of BCS theory, and especially after the experimental discovery of the superfluid phases of liquid ^3He (77), theorists explored the possibility of pairing with a more complicated orbital structure (*p*-wave or *d*-wave, for example), in which the gap can vary in both magnitude and phase with position on the Fermi surface. (In the case of odd partial wave pairing, the pairs are forced by the Pauli principle to have triplet, rather than singlet, spin wave functions.) Many of these states have nodes of the gap at points or on lines on the Fermi surface, and consequently the number of excitations in such states at low temperatures varies as a power of the temperature, rather than exponentially. Following a rather hectic 2-year period of exploration of possible states, it was established (78) that the pairing in liquid ^3He is in two distinct *p*-wave states, the A phase corresponding to the Anderson-Brinkman-Morel (ABM) state (78), which has point nodes on the Fermi surface, and the B phase to the Balian-Werthamer state (79), which has a gap of constant magnitude over the Fermi surface, but varying phase. In these *p*-wave states the pairs are in triplet states, as required by the Pauli principle, and they possess magnetic properties very different from singlet pairing states; these provided invaluable clues in the detective work to pin down the nature of the states.

Research on the superconducting phases of the heavy-fermion superconductors is currently in a period reminiscent of the years immediately following the discovery of the superfluid phases of ^3He . Theorists are studying the microscopic origin of the interactions responsible for superconductivity and the nature of the resulting pairing states, and experimentalists are searching for phenomena that may provide evidence for the nature of the energy gap.

A fundamental question in connection with the observation of superconductivity in heavy-electron systems is whether it is the heavy electrons themselves that become superconducting. Clear

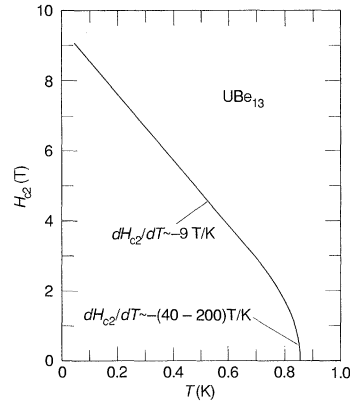
evidence for the pairing of the heavy electrons is provided by measurements of the jump in the specific heat at the transition temperature, T_c , to the superconducting phase. Quite generally in pairing theories of superconductivity, such as the BCS theory and its generalization to anisotropic states, one expects a specific heat jump proportional to the normal state specific heat of the electrons that become superconducting. The fact that the measured jumps (5, 10, 12, 13) are comparable to the specific heat in the normal state above T_c shows conclusively that the superconductivity is associated with the heavy electrons, rather than a possible band of light electrons that would provide but a small part of the normal state specific heat.

A second fundamental question is whether the superconducting energy gap has nodes on the Fermi surface, and, if so, what their character is. Experimentally, no equilibrium or transport properties in the heavy-fermion superconductors exhibit the exponential behavior expected for states with a nonzero energy gap everywhere on the Fermi surface; rather both specific heat and transport measurements display the power-law behavior that is characteristic of states with gaps that vanish at points or along lines on the Fermi surface. Specific heat measurements at low temperatures, which reflect the density of quasiparticle states at energies of order $k_B T$, give direct evidence about the nodes of the gap. At low temperature, the only quasiparticles excited will be those in the vicinity of nodes of the gap. These states possess an energy less than $k_B T$ and lie within an angle $\sim T/\Delta$ of a node, where Δ is the maximum value of the energy gap on the Fermi surface. A simple geometric argument shows that the density of quasiparticles varies as T^2 for nodes at points and as T for nodes on lines, and the corresponding variation of the specific heat is as T^3 and T^2 , respectively. In this way the experimental measurement (80) of a T^2 dependence of the specific heat for UPt_3 shows that the energy gap vanishes on a line or lines, while the T^3 dependence found (44) in UBe_{13} is indicative of a gap that vanishes at points. Thus heavy-fermion systems possess at least two superconducting states. Since UBe_{13} possesses cubic symmetry, whereas UPt_3 is hexagonal, it is possible that crystal structure plays a role in determining the nature of the superconducting state. Evidence that suggests the possible existence of two superconducting states in a single system is provided by specific heat (44) and critical field experiments (81) on $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$, where x lies between 2 and 4% (Fig. 7).

A third question of interest is where the nodes lie on the Fermi surface. Information about this is contained in measurements of transport coefficients such as acoustic attenuation. In UPt_3 the attenuation, α , of transverse ultrasound propagating in the basal plane (82) shows a different temperature dependence according to whether the sound wave is polarized in the basal plane ($\alpha \propto T$) or perpendicular to it ($\alpha \propto T^2$). These results suggest that quasiparticles move more freely in the basal plane than perpendicular to it, which would be consistent with a quasiparticle gap having nodes on lines on the Fermi surface perpendicular to the hexagonal axis. Further evidence for this behavior of the gap is provided by the recent tunneling measurements (83) that give no evidence for a gap when quasiparticles are injected across crystal faces with normals perpendicular to the hexagonal axis, but show a distinct gap when quasiparticles are injected across faces with normals parallel to the hexagonal axis.

Considerable effort has gone into trying to understand transport in the superconducting states. Under circumstances in which scattering by impurities is the dominant process, as is the case in UPt_3 at temperatures of the order of T_c and lower, the temperature dependence of the transport coefficients seems to disagree with calculations for any anisotropic superfluid state if the scattering is treated in the Born approximation. In this approximation the lowest order *s*-wave scattering by a single impurity is considered; the calculated

Fig. 8. Upper critical magnetic field H_{c2} versus temperature T for UBe_{13} .



mean free paths increase with decreasing temperature, and one finds results for the thermal conductivity, κ , and acoustic attenuation, α , that are much larger than those observed experimentally. Pethick and Pines (84) have shown that if one takes into account the multiple scattering of quasiparticles by impurities, and if one is near the unitarity limit characterized by a phase shift, $\delta \sim \pi/2$, the mean free path for electron impurity scattering shows remarkably little dependence on temperature, so that both α and κ/T fall off with decreasing temperature, in agreement with experiment. The transport data for UPt_3 , including the anisotropies observed by Shivaram *et al.* (82) in the attenuation of transverse sound, can be accounted for qualitatively if, as noted above, one has a polar state in which the superconducting gap has nodes on lines on the Fermi surface that are parallel to the c -axis of the crystal, and the mean free path is independent of temperature (85). In their calculations, Pethick and Pines (84) did not take pair-breaking into account. These effects are important only at energies close to the gap energy, Δ , and at low energies, $E \sim \hbar/\tau_n$, where τ_n is the lifetime for impurity scattering in the normal state; these have been included in the work of Schmitt-Rink *et al.* (85), Hirschfeld *et al.* (86), and Scharnberg *et al.* (87) who find in numerical calculations that with $\hbar/(\tau_n \Delta) \sim 10^{-2}$, pair-breaking effects are important for polar states only at temperatures below $\sim (T_c/10)$, in agreement with the above estimate.

In general, features around the nodes are smeared out by impurity scattering. Evidence for this physical effect on the density of states in the superconducting state of UBe_{13} has been found (88) in experimental measurements of the specific heat at low temperatures ($T \approx 50$ mK); the experimental results are in excellent agreement with theoretical calculations of the state density that assume an axial state, in which the energy gap has point nodes, and electron impurity scattering that is near the unitarity limit.

Further evidence concerning the nature of the pairing state in UBe_{13} comes from measurements of the temperature dependence of the London penetration length, $\lambda(T)$. This parameter measures the depth to which a magnetic field penetrates the superconductor, or what is equivalent, the spatial extent of the supercurrent responsible for the Meissner effect. Einzel *et al.* (89) find that $\lambda(T)$ does not exhibit the temperature dependence expected for a BCS superconductor, but rather that its behavior can be understood assuming an axial superconducting state.

To the extent that the quasiparticle wave functions reflect the strong spin-orbit coupling of the localized f -electrons in the uranium compounds, the pairing states in these metals cannot be characterized by the net pair angular momentum (s , p , d , and so forth) as is the case for liquid ^3He (78). A classification of possible pairing states based on group theoretical arguments that take into account both the specific crystalline symmetry and spin-orbit coupling has been developed by Blount (90) and Volovik and Gor'kov (91); one

interesting consequence is that for UPt_3 , the polar state must possess even parity (corresponding, say, to an anisotropic d -state pairing in the absence of spin-orbit coupling and periodic lattice effects).

There can be little doubt that the superconducting states observed in the heavy-electron systems are unconventional, when compared to typical metallic superconductors. It is therefore natural to inquire whether the physical origin of superconductivity is likewise unconventional, in that it does not arise from an attractive phonon-induced interaction between electrons. Although there is as yet no theoretical proof or direct experimental demonstration that electron-phonon interactions are essentially irrelevant to heavy-fermion superconductivity, in view of the persuasive physical arguments that the origin of the large masses is the coupling of conduction electrons to the local moment fluctuations, and that the virtual exchange of such spin fluctuations gives rise to an attractive interaction between heavy-electron quasiparticles, it would seem highly likely that it is the electron local moment fluctuation coupling that is responsible for heavy-electron superconductivity. Whether the resulting pairing state is " p -like" or " d -like" depends on the details of the wavevector dependence of the effective attractive interaction.

We call attention to three further "unconventional" aspects of heavy-fermion superconductivity:

- 1) The critical field slopes, $-(dH_{c2}/dT)$, are anomalously large near T_c , and, in the case of UBe_{13} , this slope changes substantially for magnetic fields above 1 tesla (92) (Fig. 8).
- 2) The critical fields at zero temperature are larger than the Pauli values calculated with the assumption that the heavy-electron quasiparticles possess a magnetic moment equal to one Bohr magneton.
- 3) The superconducting properties of UPt_3 are remarkably sensitive to small concentrations of impurities; for example, substitution (93) of less than 1% palladium for platinum reduces T_c to below 20 mK, and in general magnetic and nonmagnetic impurities both tend to strongly depress the transition temperature.

Concluding Remarks

The qualitative description we have of heavy-electron systems is attractively simple. At high temperatures the f -atoms behave as a collection of nearly independent magnetic moments. Because of the interaction between f -electrons and conduction electrons, at lower temperatures of order the Curie-Weiss temperature Θ_{CW} , these moments become screened by the formation of a cloud of conduction electrons with antiparallel spin. At still lower temperatures, typically of the order of $\Theta_{CW}/10$, the residual interaction between the f -electron moments leads to significant antiferromagnetic correlations among them. The interaction induced between itinerant electrons by the antiferromagnetic fluctuations associated with the correlations is responsible for the enhanced electronic specific heat and the superconducting transition. Such an interaction inhibits the usual isotropic BCS pairing state but favors anisotropic pairing states characterized by the vanishing of the energy gap at points or on lines on the Fermi surface. For these anisotropic states, unlike the isotropic one, there is no conflict between magnetic ordering and superconductivity, so that the coexistence of antiferromagnetism and superconductivity in some heavy-electron systems may be viewed as a natural consequence of the fact that a single interaction is responsible for both phenomena.

What is the relationship between heavy-electron systems, the mixed-valence compounds and the transition metals? In mixed-valence compounds d - or f -shell energy bands lie close to the Fermi surface, and the Coulomb hybridization of electrons belonging to the different energy bands plays a dominant role in determining system behavior. In heavy-electron systems, it is the magnetic

interactions between the f -electrons and the conduction electrons that are the dominant ones; to the extent that one tries to make a heavy-electron system with an f -electron band near the Fermi surface, Coulomb hybridization will inhibit the physical processes responsible for the onset of the antiferromagnetic correlations that set the stage for the appearance of characteristic heavy-electron phenomena. What makes the transition metals so interesting (and makes it so difficult to develop a first-principles description of them), is that both Coulomb hybridization and magnetic interactions play a significant role in determining their behavior.

What is the relationship between heavy-electron superconductors, "ordinary" superconductors, and the very recently discovered (94, 95) high T_c superconducting oxides? Some 37 years after the discovery of the isotope effect (96) on the transition temperature of metallic superconductors, which demonstrated the important role played by phonons in determining the transition to the superconducting state, and 30 years after the microscopic BCS theory (76), which took as its starting point an attractive phonon-induced interaction between electrons near the Fermi surface, a new mechanism for superconductivity and new superconducting pairing states in metals have been identified in the heavy-electron systems. It is natural to inquire whether the high T_c superconducting oxides belong to the same family as the heavy-electron superconductors (97); the detection of antiferromagnetic ordering (98) in pure La_2CuO_4 would seem to suggest this might be the case, but the isotropy of the energy gap inferred (99) from penetration depth measurements would appear to argue against this possibility. It took some 3 years of intensive experimental and theoretical investigations for researchers of heavy-electron materials to arrive at a consensus on the physical picture we have set forth in this article; it would not be surprising if a similar period of time might be required to arrive at a similar consensus on the new high T_c materials.

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Tropical Forests and the Global Carbon Cycle

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New data on the three major determinants of the carbon release from tropical forest clearing are used in a computer model that simulates land use change and its effects on the carbon content of vegetation and soil in order to calculate the net flux of carbon dioxide between tropical ecosystems and the atmosphere. The model also permits testing the sensitivity of the calculated flux to uncertainties in these data. The tropics were a net source of at least 0.4×10^{15} grams but not more than 1.6×10^{15} grams of carbon in 1980, considerably less than previous estimates. Decreases in soil organic matter were responsible for 0.1×10^{15} to 0.3×10^{15} grams of the release, while the burning and decay of cleared vegetation accounted for 0.3×10^{15} to 1.3×10^{15} grams. These estimates are lower than many previous ones because lower biomass estimates and slightly lower land clearing rates were used and because ecosystem recovery processes were included. These new estimates of the biotic release allow for the possibility of a balanced global budget given the large remaining uncertainties in the marine, terrestrial, and fossil fuel components of the carbon cycle.

THE CONCENTRATION OF CARBON DIOXIDE IN THE ATMOSPHERE has increased from about 280 parts per million (ppm) circa 1750 to about 345 ppm in 1984 (1). Because CO_2 and other trace gases (for example, methane, nitrous oxides, and chlorofluorocarbons) produced by industrial and agricultural processes absorb thermal radiation emitted by the earth's surface (2), researchers have predicted that the increasing concentrations of these gases in the atmosphere will result in significant changes in climate (3), which in turn may produce substantial changes in the location of agricultural zones and shorelines (4). Because the effects of CO_2 on climate are in some dispute (5), determining how carbon cycles among the atmosphere, hydrosphere, and biosphere is of continuing interest.

Since 1977 this interest in the global cycling of carbon has involved a controversy between terrestrial ecologists and geochem-

ists. All participants agree that the principal cause of the increase in atmospheric CO_2 in recent years has been the combustion of fossil fuels, which released about 5.2 gigatons (GT; $1 \text{ GT} = 1 \times 10^{15} \text{ g}$) of carbon during 1980. The kilning of limestone for the production of cement released an additional 0.1 GT, for a total of 5.3 GT from industrial processes in 1980 (6). But long-term studies of atmospheric CO_2 conducted at Mauna Loa since 1958 indicate that only 55 percent of the CO_2 released from industrial activities remains in the atmosphere (7). The most likely repository of some or all the remaining 45 percent is the oceans. Because it is not possible at present to measure directly the increase in inorganic carbon dissolved in seawater (8), estimates of the ocean's uptake of CO_2 have been based on models, most of which predict relatively small oceanic uptake (9). Present versions of these models estimate that the oceans sequester approximately 35 percent of the CO_2 released by industry (10). To balance their global carbon budgets, a number of geochemists postulated that terrestrial ecosystems, like plants in greenhouses, increase their rate of photosynthesis in the presence of increasingly elevated levels of CO_2 (11).

In 1977, however, several terrestrial ecologists concluded that not only was it unlikely that terrestrial ecosystems would increase their carbon storage in response to increased atmospheric CO_2 but that the destruction of these ecosystems, primarily tropical forests, was releasing nearly as much CO_2 into the atmosphere as were industrial processes (12). In their view, the oceans were the only likely sink for both the fossil fuel CO_2 not found in the atmosphere and the CO_2 released from forest clearing (12, 13). Two early studies suggested that the annual releases from forest clearing could be as large as two to four times those from fossil fuels and limestone (14), although these estimates were later revised downward (15). The geochemists, however, believed that their models of oceanic CO_2 uptake were sufficiently accurate to exclude the possibility of such a large error in their estimates, and they attacked both conclusions of the ecologists. They argued that too little was known about rates of forest

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