Accumulating insight into the properties of heavy-electron (or heavy-fermion) metals is raising as many questions as answers among the condensed-matter physicists who study them.

Not too long ago, scientists tilling the field of solid-state physics were entitled to feel somewhat self-confident, more or less the way particle physicists felt around 1930, before a tidal wave of subatomic particles inundated them.

In 1981, for example, Theodore H. Geballe, director of the Center for Materials Research at Stanford University, was asked to review the discipline for a special issue of Physics Today on the previous 50 years in physics. He titled his article, appropriately, "This golden age of solid-state physics," and it began this way:

Michael Faraday [in 1843] was surprised to find the resistance of silver sulfide went down when the temperature went up; Hans Meissner [in 1929] was surprised to find that copper sulfide suddenly became a much better conductor than metallic copper at very low temperature [two degrees Kelvin]. People through the ages have puzzled over why the compass does what it does. We now have a fairly fundamental understanding of why these things happen. Solid-state physics has been able to show how real materials governed by the laws of quantum mechanics can behave in such a variety of ways.

Today, that roseate view must be altered. Within the last five years, the discovery and subsequent investigation of strange materials with bizarre properties have shattered the complacency of solid-state physicists. To borrow an Oxford University particle physicist's reply to a heckler's impertinent challenge about the state of his field: "We're in a mess, [and] we're trying to understand the mess we're in. We're doing the best we can. If you can do any better, then by all means do, but it's hard."

These strange materials are known as heavy-electron intermetallic compounds, or systems. (Electrons belong to the class of subatomic particles known as fermions.) Electrons, of course, are not heavy, having only about one eighteen-hundredth of the mass of a proton. However, in these materials they perform as if they were heavy indeed, and had up to a thousand times the mass of a normal electron.

They display this anomalous heavity through a number of properties, especially specific heat, which in these materials is orders of magnitude higher than it should be. (Specific heat is a measure of the heat required to raise the temperature of a given mass of a substance by a specified amount. For example, it takes one calorie to raise the temperature of one gram of water at room temperature and pressure by one degree centigrade.)

An even more startling feature of a few of these materials is that they turn into superconductors at temperatures near absolute zero, which, under all previously accepted rules, they have no business doing. This leads theorists to wonder whether they are encountering an entirely new form of superconductivity that cannot be explained by even the best previous model.

These discoveries are contributing to considerable upheaval in the arena of what is now called condensed-matter physics. This rubric includes liquids, some kinds of gases, and solids, and has increasingly replaced the term solid state. ("This is not a bad thing," writes N. W. Ashcroft of Cornell University, "for it more accurately describes the drift toward studies of matter that on the one hand display manifestations of order that are often quite dramatic, and yet very often show no vestige of the crystalline perfection we normally take to be the imprimatur of the solid state."

Heavy-fermion systems, Theodore H. Geballe wrote in 1983, "offer us a rich new playing field." But it is a field on
which a game is unfolding in which the rules remain opaque and puzzling. For roughly 50 years, physicists have relied on two simple pictures—simple to the point of caricature—of how electrons behave in solids. One picture portrayed a kind of sea of electrons free to propagate through the solid without much hindrance from the atoms. Such electrons, called itinerant, are able to carry electric current in metals. The other picture described electrons that were generally bound to their individual atoms. Such electrons, called localized, played a different role in solids, contributing to magnetism through their spins.

Today, however, physicists are compelled to conclude that these two pictures are inadequate, for the behavior of heavy-fermion materials fits neither. Either these pictures must be modified, or a completely new third picture must be painted.

The odd players in this game—ten so far—are intermetallic compounds, with at least one constituent being either a lanthanide (rare earth, such as cerium) or an actinide (such as uranium) atom with certain electron shells (numbered 4f or 5f) partially filled.

Aberrant properties

Materials with partially filled shells traditionally fall into one of three classes: metals, semiconductors, or Mott insulators (named after Nevill Mott, a 1977 Nobelist in physics). The heavy-fermion materials do not fit in any of these three categories; rather, they exist in a phase that is neither Metastable nor Insulator.

Tantalizingly different from conventional and well-studied rare-earth and actinide compounds.

At high temperatures, these conventional compounds act as if their f electrons were localized at their atomic locations, thus giving rise to magnetic moments. Itinerant electrons in these compounds come from loosely held s, p, and d shells. If they are cooled, the magnetic moments contributed by the f electrons line up in an ordered fashion, forming a magnetic ground state (mostly antiferromagnetic, but sometimes ferromagnetic).

The heavy-fermion compounds, on the other hand, do not follow this well-understood transition. When cooled, they form an itinerant or delocalized metallic state with aberrant properties. Their low-temperature specific heats and magnetic susceptibilities show that some of the f electrons have indeed become conduction or itinerant electrons (like the current-carrying electrons in normal metals), but the values for these properties are two to three orders of magnitude higher than those for ordinary metals. The startling implication is that they also have masses that are orders of magnitude larger than normal.

It is probably more accurate to refer to these entities as quasi-particles. "Obviously, we are not dealing with a new kind of elementary particle," says Frank Steglich, of the Institute for Solid-State Physics at the Technical University of Darmstadt, Germany. "Instead, the heavy fermions represent low-energy excitations of a strongly correlated (many-body) ground state. It is widely assumed by now that in the low-temperature phase of heavy-fermion systems, extremely strong correlations between conduction electrons develop as a result of a very strong interaction of the delocalized carriers and another species of electrons, which are well localized within the cores of the lanthanide or actinide atoms. The quasi-particles can therefore be considered as conduction electrons which are 'heavily dressed' by their interaction with the f electrons and consequently will move relatively slowly through the lattice."

Superconductivity

Even more baffling is the behavior of three of the heavy-fermion compounds and cerium copper 2 silicon 2, uranium beryllium 13, and uranium platinum 3. When cooled they become superconductors, a phenomenon totally at odds with the modern theory of superconductivity—the BCS theory (named after three physicists—see below). The reason: Superconductivity should be incompatible with magnetism.

The Argonne National Laboratory's A. J. Arko gave the prevalent view of heavy fermions at an American Physical Society meeting in March 1986: "One would normally anticipate that such [heavy] electrons would be involved in causing magnetism [because they are localized at normal temperatures, giving rise to magnetic moments]. Yet, not only do they carry current . . . in their sluggish fashion, but in some instances the materials actually become superconductors at low temperatures. Some heavy fermions do . . . become magnetic [uranium 2 zinc 17, for example].

"It is the superconducting feature, however, which causes most of the excitement in the physics community, since it would appear that we are not dealing with the ordinary type of superconductivity . . . Indeed, there seems to be a coexistence of magnetic and superconducting behavior which is incompatible with ordinary BCS superconductivity. Irrefutable proof that we are dealing with non-BCS superconductivity has been elusive, but it is of fundamental importance to solid-state physics."

The phenomenon of superconductivity was revealed in dramatic fashion in 1911 by the Dutch physicist Heike Kammerlingh Onnes. Experimenting with the effects of very low temperatures on a variety of materials, he was astonished to find that all resistance to the flow of electricity in mercury suddenly dropped to zero at about 3 degrees Kelvin. Onnes started a current flowing in a conductor in the shape of a closed loop, kept it refrigerated, and quarantined it from any external electrical or magnetic influences. A year later, the current was still flowing at its original strength.

Nearly half a century elapsed, however, before science found a palatable explanation of what was actually occurring inside a superconductor on a microscopic scale. In 1957, three physicists at the University of Illinois—John Bardeen, Leon N. Cooper, and J. Robert Schrieffer—proposed what is now the BCS theory, named after the first letters of their last names. It hinges on postulating the formation of pairs of electrons called Cooper pairs in superconductors (Cooper had conceived of such pairs the year before).
In most metals and alloys, the flow of conduction electrons through the crystal lattice, a regular array of positive ions (atoms that have lost electrons), is hindered by collisions with two sets of obstacles, one static and one dynamic. The static impediments are imperfections in the orderly array of the lattice: holes, grain boundaries, dislocations, and the presence of impurities known as dopants. The dynamic obstacles are heat-induced vibrations of the lattice, known as phonons.

However, as the temperature is lowered, a phonon-mediated, attractive interaction between electrons leads to the formation of pairs of electrons with opposite spin. Each such Cooper pair is actually much larger in diameter than the average distance between conduction electrons, and hence each electron effectively belongs to a very large number of overlapping pairs. As a result, the electrons' motions (but not their positions) become highly correlated and acquire a kind of rigidity that allows them to sweep through the crystal lattice unhindered; all resistance to the passage of current has disappeared.

But the presence of a magnetic state would destroy superconductivity, according to the BCS theory. The magnetic field would disrupt the Cooper pairs, cancelling the superconductive properties. Hence the shock at witnessing superconductivity in the heavy-fermion materials containing their magnetic-moment-contributing f electrons. Frank Steglich notes that ordinary superconductors discovered were originally reported as footnotes, because they were so unbelievable. Smith heads the Physical Metallurgy Group of the Materials Science and Technology Division at Los Alamos, and with colleagues Zachary Fisk and Jeffrey O. Willis, has done pioneering work in the discovery of new heavy-fermion systems.

"In 1974," Smith says, "Ernst Bucher at Bell Labs was doing low-temperature experiments with a family of compounds that had magnetic moments, including rare earth beryllium 13s, and uranium and thorium beryllium 13s. One day, he noticed that uranium beryllium 13 went superconducting at a certain temperature. But he was a very good materials guy—he knew superconductors—and so he knew that was utter nonsense. You put an enormous magnetic field on it, and the critical temperature hardly changed. So he said that there must be something wrong with the sample, which he hadn't prepared himself—some impurities at the grain boundaries.

"At the time, that suspicion was very logical, and in a footnote to a paper Bucher duly reported that the material had gone superconducting, and what he thought the problem was, allowing the whole thing to be forgotten."

The second case of this kind of accidental discovery going unrecognized—indeed, merely being footnoted—came in 1977. A group of researchers in Cologne, including a young scientist named Frank Steglich, were investigating cerium copper 2 silicon 2. It became a superconductor at low temperature. "And again," says Smith, "that was complete nonsense. All of its properties were those of a conductor. The group reported what had happened in a footnote to their paper, but again said there was obviously something wrong because it just couldn't be a superconductor. Steglich, however, continued to investigate the compound, because he was not satisfied. There was no consistency; some samples went superconducting, some didn't. It was really hairy. And the senior man of the group kept saying, 'Frank, don't work on this. You'll spend five years of your life until you learn what's going on and then it won't even be interesting.' But it took only two years—till 1979—for Steglich and some colleagues in Darmstadt to demonstrate convincingly that the peculiar cerium compound was, in fact, a heavy-fermion superconductor. This was the first to be so proven.

The second such compound to be rescued from footnote status, uranium beryllium 13 was observed because of a collaboration between the Los Alamos group and Hans Ott and colleagues at the Eidgenössische Technische Hochschule in Zürich. Ott had been investigating heavy-fermion cerium compounds that had very heavy electron masses at low temperatures, but did not go superconducting. (One of them is cerium aluminum 3, which is even heavier than cerium copper 2 silicon 2.) When he came across Bucher's original footnote on uranium beryllium 13, he became curious.

A megacrystal

"They don't work on beryllium in Switzerland," says Smith, "because they once had a nasty accident with it at the University of Geneva. Beryllium is very toxic. So Ott called Zachary Fisk here at Los Alamos to see whether we'd done anything. Here, we work with plu-

Fisk. Metallurgical magician with crystals.
tanium, so we can handle anything. Hans wondered if it could really be true that the uranium compound went superconducting. We didn’t do anything about it until 1982, when Ott wrote suggesting that maybe UBe_{13} had the very same superconducting properties as CeCu_{2}Si_{2}.

“I’m used to making polycrystals by melting metals together in a welder’s arc furnace. So I made a little bead of UBe_{13} polycrystal and went to check it. Zachary came in and I said to him, ‘It’s superconductive, just like the footnote said,’ and he said ‘Give me that’ and went off to make a single crystal. Then I made a bigger bead, which was superconducting too, cut it in half, and sent half to Ott. Zachary,” he recalls, “snatched the other half.”

Zachary Fisk has been called a metallurgical magician for his ability to grow large single crystals of materials that prove to be intractable for many other experimenters. The advantage of growing single crystals is that they are pure, with all of the atoms nicely lined up. There are no grain boundaries or impurities—nothing dirty to alter the material’s intrinsic properties. Bucher’s original uranium beryllium 13 sample was polycrystalline however, possibly making its superconductivity unrepresentative.

“Just two days later,” Smith recalls, “I found Zachary pointing a flashlight beam into a crucible. ‘I don’t believe it,’ he says, and puts the flashlight down. I picked it up and shone it into the crucible. And there was this whole facet—it looked like the Hope diamond—the bottom of the crucible was one big shiny surface. It was a single crystal, and when we tested it, it went superconducting. So then, there was no question.”

Indeed, the second heavy-fermion superconductor (actually the first that was observed) had been confirmed.

The third was not long in coming. Within a few months, Fisk’s deft techniques were focused on making single crystals of compounds that had the same crystal structure as the heavy-fermion compound cerium aluminum 3, which Hans Ott was investigating. One of these compounds was discovered to be uranium platinum 3.

“Zachary started working on it,” says Smith, “growing little whiskers of pure single crystal, and then subjecting them to low temperatures. At one degree Kelvin, the resistance was still dropping. He wanted to know how low it could get, so he gave one to Jeff [Jeffrey O. Willis] to test at still lower temperatures. One Friday in September 1983, Jeff saw the resistance go to zero—the damn thing went superconducting! Zachary couldn’t believe it, and I said, ‘oh my God! We got two like this.’ For various reasons we thought there would then be a whole lot more of them, but there haven’t been, and we’ve worked hard to find them. We’ve found more heavy things, and Zachary and Hans Ott quickly found that some of them were also magnets.

“The problem is, what in the world is going on microscopically? It’s clear that all these heavy things are very strange animals. The ones that become magnetic are different from all other magnets. This is a new class of materials—a new class of phenomena. The theorists are working on that. We are experimentalists.”

**Hard theory**

The theorists are having a hard time. As one of them, a Nobel laureate, said recently, “Unification theory isn’t hard, chaos theory isn’t hard, heavy-fermion theory is hard!”

There is speculation, for example, that the three heavy-fermion superconductors are displaying a triplet rather than a singlet type of superconductivity. Singlet is characteristic of all other known, i.e., conventional, superconductors. The Cooper pairs of the original BCS theory are in a singlet state that has no internal degrees of freedom. Because the electrons in the pair have opposite spin, the total spin is zero.

In the triplet Cooper pairs, the spins are not opposite and add to one, giving three degrees of internal freedom, or a triplet state. That is the state of the pairs in superfluid helium 3. This substance loses all viscosity at a temperature close to absolute zero, suggesting an analogy to the loss of electrical resistance in conventional superconductors. Is it possible that heavy-fermion experimenters have actually discovered triplet superconductivity?
With its three degrees of freedom, a triplet superconductor should theoretically be anisotropic, that is, its superconducting characteristics should not be identical for each of three crystal axes. Such anisotropies have been found in experiments by Steven E. Lambert of the University of California at San Diego, who is investigating the relationship between temperature and the critical magnetic field (the point at which the field destroys superconductivity), and in experiments by David J. Bishop, of Bell Labs in Murray Hill, New Jersey, who is investigating the absorption of ultrasound.

But, as Kazuo Ueda of the Department of Applied Physics of the University of Tokyo says, "At present there is no consensus in the literature on the interpretation of experimental results."

The "smoking gun" for triplet superconductivity has not appeared on stage.

Similarly, there is no consensus on the basic problem of what causes the anomalous properties of heavy-fermion systems—or rather, there is no consensus on whether there is a consensus.

In 1985, Fisk, Smith, and Ott wrote: "It is fair to say that no consensus of any kind exists as to a proper theoretical description of the heavy-fermion ground state. . . ."

One long-time observer of the field, who wishes to avoid controversy and remain anonymous, says bluntly: "It's a mess. It's like the blind men and the elephant, except we don't even know whether there is an elephant. There are no universally accepted explanations for heavy fermions. We can't get any agreement on why they are heavy or on what the mechanism for their superconductivity is. We can't even get the same people to look at the same data and come to the same conclusions.

From there on . . .

"One of the basic problems is the concept of a single impurity in metals, which goes under the generic name of the Kondo problem, which is also called the Anderson model. . . . It took 20 years for that model to finally settle down—it's been around since 1964—and we finally started getting general agreement in the last couple of years. That's a long time for a problem to stay unsolved. It has a lot of bizarre features, not all of which have been observed. But now a fairly simple physical picture exists for it.

"Now some theorists want to take a
Shells and states

In quantum mechanics, two distinct sets of particles obey two different kinds of statistical laws that govern their distribution. Bosons (named for Satyendra Nath Bose, an Indian physicist and mathematician) include photons and pi mesons, have integer spin, and obey Bose-Einstein statistics. Fermions, named for Enrico Fermi, include electrons, have half-integer spin, and obey Fermi-Dirac statistics. They also obey Wolfgang Pauli's exclusion principle, which says that no two fermions in an atom may occupy the same quantum state.

It takes four quantum numbers to describe an electron orbiting an atomic nucleus: The principal quantum number, $n$, specifies the shell, or energy level, that the electron occupies; the azimuthal quantum number $l$, defines the shape of the orbit within the shell; the magnetic quantum number, $m$, determines the orientation of the orbit within the context of a high magnetic field; and the spin quantum number, $m_s$, indicates the direction of the electron's spin about its own axis (conventionally called spin up or spin down) in a magnetic field.

Quantum theory states that the principal quantum number can be any positive integer; the azimuthal number can be any positive integer up to and including the principal quantum number minus one; the magnetic number can be any integer lying between the positive and negative values of the azimuthal number; and the spin number can be either plus 0.5 or minus 0.5.

As applied to an atom, the Pauli exclusion principle states that no two electrons can have exactly the same four quantum numbers. In the lightest and simplest atom—hydrogen—there is only one electron orbiting a single proton. The principal quantum number is the lowest allowed, one, which corresponds to the lowest energy state, known as the ground state. Helium has two protons and two electrons. These two can share the ground state (i.e., the first orbital shell), because even though three of the four quantum numbers are identical, the fourth—spin—is not. One electron can be spin up, the other spin down. Because there are only two options for the spin quantum number, however, no more electrons can occupy that shell; it is filled at two. Lithium's third electron, therefore, must differ in one of the other quantum numbers, which forces it into a shell at a higher energy level.

Generally speaking, as the elements increase in atomic number, the added electrons must fill shells and then occupy quantum states of ever-higher energy. (The uppermost occupied state—the highest energy level—is called the Fermi level, a concept that was extended by Hans Bethe to become the Fermi surface.) Pauli's exclusion principle governs the number of electrons that can fit in each shell, and this gave rise to the notion of patterns that allowed Mendeleev (and some others) to arrange a table of the elements systematically.

These shells, or orbital states, are designated by a number and a letter. The number corresponds to the principal quantum number. The letter corresponds to a geometrical property of the electron density probability in that shell. The letter $s$ represents the simplest, spherical state; $p$, $d$, and $f$ represent more complex geometries. (These are actually the initial letters of the words sharp, principal, diffuse, and fine—each of which refers to a different group of spectral lines, which in turn correspond to different quantum states.)

What is relevant to the story of the heavy-fermion compounds is that there is a certain precedence to the filling of shells: It begins 1s, 2s, 2p, 3s, 3p, but then hops: 4s, 3d, 4p, 5s, 5p and so on, creating so-called transition elements such as iron, nickel, and cobalt. These have a partially filled inner shell, the 3d, which plays a key role in ferromagnetism. Similar skips occur further up the periodic table, resulting in lanthanides with partially filled 4f shells and actinides with partially filled 5f shells, while shells that are located farther out are already occupied with fixed numbers of electrons.
lot of those models and make a lattice of them to explain heavy fermions. The problem is how you do that. Many people would like to say the single impurity basically dominates most of the properties, skipping the details. Others say that's absolute rubbish, that the interactions between those impurities completely dominate the properties of the whole, and that's completely different physics. And there we are."

The Kondo referred to by Smith, Fisk, and Ott is a Japanese physicist, J. Kondo, who in 1964 explained a peculiar anomaly: a small concentration of paramagnetic (3d, 4f, or 5f) ions dissolved in a metal can cause an increase in electrical resistivity with decreasing temperature. The effect was first observed in slightly impure gold, using iron (with its unfilled 3d shell) as the impurity. In this instance, the localized magnetic moment of the impurity's d or f atoms interacts with the opposite spin of the conduction electrons. However, the concentration of the impurity is so dilute—a single ion in the Kondo model—that the effects are purely local.

In the heavy fermions, one theory holds, a resonance develops in the electronic density of the states at the Fermi level. Extra states will keep adding on until they accumulate there to yield a very large electronic specific heat.

The Anderson model is that of Philip W. Anderson, now of Princeton University, who shared in the 1977 Nobel Prize for physics for his work on electron localization while at Bell Labs. In December 1986, before traveling to India for a major meeting on heavy fermions the next month, he said, "I'm throwing away my text to the effect that there is no good, coherent theory to explain heavy fermions, and am going to say that people are arriving from different directions at the same ideas. None of them can be called a theory yet. But my general feeling is that we are all saying very similar things.

"One, heavy fermions really do fit within the general theory of metals, the so-called Landau-Fermi liquid theory. . . . My own feeling is that all of us are going to believe it applies in a fairly straightforward way, but only in the very-low-temperature region, and with crazy values for all the parameters.

"Second, I think everyone would pretty well agree on the model you would start from, which is a lattice of so-called Anderson models, generally with a few bells and whistles added, because the materials are very chemically complicated. The Anderson model can be solved exactly, and certain things in that solution resemble the things in heavy-electron metals. The resemblance is like a distant relationship rather than a close one. . . . But what I really begin to understand now is that there are big modifications that come from the interactions. They change lots of things in detail.

"In particular, the role of the free electrons for the metal in the heavy-fermion material is taken by the entities that are mixtures of free electrons and localized electrons, things called quasi-particles rather than real particles. They are very much a complicated many-bodied mixture of all kinds of stuff in the heavy fermions. There are a lot of modifications that come from the interactions, and people are only beginning to understand how important the modifications are.

"Finally, many people are realizing that there are very strong antiferromagnetic correlations between the spins in the localized orbits of the Anderson models and that these play a very important role.

"From there on, it tends to get a bit complicated."

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