Heavy-fermion superconductors

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Usp. Fiz. Nauk **147**, 767–779 (December 1985)

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1. INTRODUCTION

So-called heavy-fermion superconductors have recently attracted a great deal of interest in low-temperature physics, primarily because of their anomalous behavior in many ways. It has in fact been suggested that these superconductors represent a fundamentally new class of superconductors in which, in contrast with all previously known superconductors, with a singlet BCS (Bardeen-Cooper-Schrieffer) superconductivity, there is an anomalous pairing of electrons which is very anisotropic and which—possibly—occurs in a triplet state. If this is the case, then the superconductivity in these systems might be similar to the superfluidity of ^{3}He, with its exotic features. Even if this turns out not to be the case, however, the richness and variety of the properties of these systems in both their superconducting and normal phases undoubtedly justify the attention they have attracted.

The present note is based in part on the proceedings of a session of the Commission on Superconductivity of the Academy of Sciences of the USSR, in November 1984 which was devoted to a discussion of heavy-fermion superconductors. We make no claim that we are attempting anything like a complete review of this new but rapidly developing field. Our purpose is to draw a general picture of this interesting class of substances and to bring them to the attention of a broader range of specialists.

2. HEAVY FERMIONS

Heavy-fermion systems are compounds of rare earth metals and actinides with an unstable 4f or 5f shell. In contrast with, say, typical rare earth compounds, in which the filled 4f levels lie far below the Fermi level, and the 4f shell is stable and filled by an integer number of electrons, the f level in heavy-fermion systems lies closer to the Fermi level, and the situation is one of an unstable valence. As a result, electron states at the Fermi level can acquire an f-state nature, and their properties can change significantly. In particular, so-called mixed-valence compounds (Ref. 1, for example) fall in this class. In the simplest picture, the f level itself lies directly near the Fermi level, and because of its smearing into the band (because of a hybridization with conduction electrons), a substantially elevated state density $N(0)$ arises at the Fermi level. The f-level itself is only partially filled; thus the term "mixed valence." However, even if the f level is still relatively deep, the properties of the electrons near the Fermi level ε_F may be renormalized substantially by virtue of collective effects of the Kondo type, i.e., a resonant scattering of conduction electrons by localized magnetic moments of f centers$^{1)}$ (Refs. 2 and 3). In either case, the state density of the Fermi level increases substantially, $N(0) \sim \frac{1}{\Gamma}$, where Γ is the effective width of the "f band." Actually, we have $\Gamma \sim 10^{-2}$–10^{-3} eV in these systems; i.e., the state density which arises is typically two or three orders of magnitude higher than in ordinary metals. In other words, the effective electron mass m^* is substantially greater than the mass of the free electron; hence the concept of "heavy fermions." The actual nature of the appearance of heavy fermions has not yet been finally resolved. It clearly involves the presence of a rather unstable 4f or 5f shell and the resulting partial collectivization of f electrons. In other words, it is related to the circumstance that states at the Fermi level partially acquire an "f nature," with the tendency toward localization and a large mass which are characteristic of f electrons. It is not clear, however, whether this is related to simply a transition of the f level itself to the Fermi level or is due to collective effects. We will not go into those questions

0038-5670/85/121136-08$01.80

here; we simply note that, purely phenomenologically, these compounds behave as materials with an exceedingly narrow band at the Fermi level, with a correspondingly high state density. (Although in the Kondo-lattice model, for example, this state density itself is of a collective nature and depends on the temperature.[2]) At temperatures $T \ll T_f$, however, where T_f is some characteristic temperature (of the order of the Kondo temperature T_K, say), the system behaves as a Fermi liquid with properties determined by T_f and $N(0)T_f^{-1}$.

At low temperatures, all the properties of the material, both thermodynamic and kinetic, are determined by specifically those electrons which lie near the Fermi surface. It is thus clear that such a pronounced change in the state density $N(0)$ should have important manifestations in all the properties of such systems. The quantity which characterizes $N(0)$ most directly is the electron specific heat,

$$C = \gamma T.$$

While in an ordinary metal we would have $\gamma \approx 1$ mJ/(mole·K^2), and in an ordinary transition metal we would have $\gamma \sim 10$ mJ/(mole·K^2), in a heavy-fermion system γ reaches values such as $\gamma \approx 1000$ in $CeCu_2Si_2$, $\gamma = 1100$ in UBe_{13}, and $\gamma = 1620$ in[3] $CeAl_3$ (in units of millijoules per mole per kelvin squared). The magnetic susceptibility is correspondingly large ($\sim 10^{-3}$–10^{-2} cgs units). There is a good summary of the experimental data on these "record-setting" compounds with heavy fermions in Ref. 4. It is already clear that these systems are extremely similar to typical magnetic compounds: The f electrons in them are substantially localized, forming an exceedingly narrow band under favorable conditions. Even more surprising is the circumstance that among the materials of this class there are some compounds which exhibit superconductivity. Superconductivity was first demonstrated reliably[5] in $CeCu_2Si_2$ back in 1979; see Ref. 4 for a more-detailed history. For some time, this discovery caused no particular stir. The commotion began after two other superconductors in this class were discovered [UBe_{13} (Ref. 6) and UPt_3 (Ref. 7)], and a study of their properties led to the suggestion[8–10] that the superconductivity in these materials was not an ordinary superconductivity and that it might be analogous to p pairing in ^{3}He [we will speak in terms of "p pairing" below, although a careful analysis[11,12] shows that this terminology is imprecise here (more on this below)].

Just what are the basic features of the superconductivity in these systems which have forced the suggestion of a possible nonstandard pairing? What is the experimental situation in research on these systems at the moment?

Several compounds have now been identified which can be classified more or less confidently as heavy-fermion superconductors. The foremost examples are the compounds which we have already mentioned: $CeCu_2Si_2$($T_c \approx 0.6$ K, $\gamma = 1000$),[4] UBe_{13}($T_c \approx 0.95$ K, $\gamma = 1100$) and UPt_3 ($T_c = 0.5$ K, $\gamma = 450$) (Ref. 4).

In addition, there are compounds of U [U_2PtC_2($T_c = 1.7$ K, $\gamma = 75$),[13] URu_2Si_2($T_c = 1.5$ K, $\gamma = 75$) (Ref. 16), URu_2Si_2($T_c = 1.5$ K, $\gamma = 75$) (Ref. 14), and U_6Co($T_c = 2.3$K, $\gamma = 21$) (Ref. 15)] and also α-U itself (at pressures $P \gtrsim 10$ kbar, $T_c = 2.1$ K, $\gamma = 12$).[17]

We see that there is an entire range of related compounds, with variations of the electron specific heat and, correspondingly, the electron mass over broad ranges. Just which of these systems should be classified as heavy-fermion systems is an open question at this point.

Among the compounds of Ce there is also a group of materials in which the value of the effective mass varies gradually from one material to the next. In addition to $CeCu_2Si_2$, superconductivity has been observed in $CeRu_3Si_2$($T_c = 1$ K, $\gamma = 39$) (Ref. 18); in the Laves phases of $CeCo^2$, $CeFe_2$, $CeRu_2$, and $CeOs_2$ (in $CeRu_2$, for example, we find[19] $T_c = 6$ K and $\gamma = 23.3$); in $CeOs_2$ ($T_c = 1.1$ K, $\gamma = 22$; Ref. 20); and in α'-Ce ($P \gtrsim 50$ kbar, $T_c \lesssim 2$ K, $\gamma = 14$; Ref. 21).[5]

The exotic record-setting systems $CeCu_2Si_2$, UBe_{13}, and UPt_3 are at present enjoying the limelight, but it may prove extremely useful to carry out a comparative study of this entire range of compounds, which provide a "smooth interpolation" between ordinary superconductors such as α-U and exotic systems like UBe_{13} and UPt_3.

The discussion below is restricted to the properties of the record-setting compounds. Two questions arise in an analysis of these compounds: To what extent are heavy fermions involved in superconducting pairing? What features of the superconducting state which arises lead to the suggestion of, in particular, a possible nontrivial pairing? We begin with the first of these questions.

3. WHICH ELECTRONS ARE INVOLVED IN THE SUPERCONDUCTING PAIRING?

Direct measurements of the discontinuity in the specific heat at T_c show that heavy fermions are indeed involved to a substantial extent in superconducting pairing. It has been found that not only is the specific heat itself, $C_n(T_c) = \gamma T_c$, huge, but the discontinuity in the specific heat at T_c is also large, so that the ratio $\Delta C/\gamma T_c$ is not greatly different from the prediction of the BCS theory, 1.43 (although, generally speaking, there is no reason to expect that this relation would hold accurately in systems with an anomalous pairing). In $CeCu_2Si_2$ we find $\Delta C/\gamma T_c \approx 1$ (this ratio, like other superconducting properties of $CeCu_2Si_2$, depends strongly on the method by which the sample is grown, the stoichiometry, etc.). In UBe_{13} we find $\Delta C/\gamma T_c \approx 1.4 - 2$, and in UPt_3 we find UPt_3 $\Delta C/\gamma T \approx 1$ (Ref. 4).

Another piece of evidence indicating the participation of heavy fermions in superconductivity is the behavior of the upper critical magnetic field. All these systems are strong type II superconductors, and their critical fields H_{c2} are large. The values of $\partial H_{c2}/\partial T$ are 230 kOe/K in $CeCu_2Si_2$, 440 kOe/K in UBe_{13}, and 40–63 kOe/K in UPb_3 (Ref. 24; in the hexagonal UPt_3 crystal and the tetragonal $CeCu_2Si_2$ crystal, there is a significant anisotropy of H_{c2}). If we use $\partial H_{c2}/\partial T$ in the standard way to estimate the effective mass, working from the Gor'kov relation[22]

$$\gamma \approx -2.21 \cdot 10^{-5} \frac{\partial H_{c2}}{\partial T} \frac{1}{\rho},$$

where ρ is the resistance in ohm·centimeters, γ is in ergs per cubic centimeter per square kelvin, and $\partial H_{c2}/\partial T$ is in oerst-

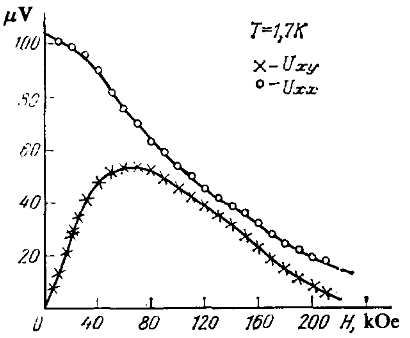

FIG. 1. The Hall voltage and the magnetoresistance of UBe_{13} as functions of the field at $T = 1.7$ K.

eds per kelvin, we find values which correspond in order of magnitude with those found from the specific heat ($m \approx 200\ m_0$) The values of $H_{c2}(0)$, on the other hand, are usually well above the paramagnetic limit.

These results thus seem to tell us that the heavy component is involved in superconducting pairing and is dominant in such properties as the jump in the specific heat, ΔC, and $\partial H_{c2}/\partial T$. On the other hand, we apparently cannot yet draw the conclusion that it is the heavy fermions which are responsible for the actual onset of superconductivity. In addition to the heavy component in these systems, there are apparently "light" electrons, of ordinary broad bands, at the Fermi level. This conclusion is implied by an analysis of data on several properties in the normal phase: the compressibility, the thermal expansion, and the thermoelectromotive force.[23] There is also direct experimental proof of the existence of two groups of electrons with very different masses: results from a study [24] of the De Hass–van Alphen effect in $CeSn_3$. Figure 1 shows measurements of the Hall effect in UBe_{13} in strong fields.[25] These results may be interpreted as evidence for the existence of two groups of carriers. On the basis of the usual concepts it might be suggested that in weak fields, where the heavy component is not manifested, the Hall emf is due to a light component with a low concentration, while in strong fields, where heavy electrons come into play, the resultant effective electron concentration increases, causing a decrease in the Hall constant. On the other hand, we do not rule out another interpretation, which has the structural features in the Hall effect in heavy-fermion systems stemming from a special mechanism for the scattering of the electrons of the broad bands by a narrow f resonance near the Fermi level.[48] In that interpretation, however, it is actually again assumed that there are two groups of electrons with very different masses.

It can thus apparently be assumed that electrons of two types, heavy and light, coexist in heavy-fermion systems. At this point we cannot conclude from the data we have seen here on ΔC and $\partial H_{c2}/\partial T$ that it is the heavy fermions and the interactions characteristic of them which are responsible for the superconductivity: Even if superconducting pairing were due to the attraction of "light" electrons, through a hybridization and an interaction with the heavy component, the "heavy" mass would still be manifested in such quantities as C_n, ΔC, and $\partial H_{c2}/\partial T$. On the other hand, the light component might (and apparently actually does) make its presence known in several superconducting characteristics. In an ordinary single-component system, for example, the London penetration depth is $\lambda_L^2 \approx m^* c^2/4\pi n_s e^2$, and for $m^* \sim (200\text{–}400) m_0$ the value of λ_L would be large. Experimentally, however, according to measurements of the thermodynamic critical field H_{cm} and the Ginzburg-Landau parameter $\varkappa$ (Ref. 26), the London penetration depth in UBe_{13} is $\lambda_L = 3.6 \cdot 10^{-5}$ cm; i.e., it is of the order of magnitude characteristic of ordinary superconductors. In the compounds WBe_{13}, where $m^* \sim m_0$, we find $\lambda_L = 2 \cdot 10^{-5}$ cm; this value is extremely close to the penetration depth in UBe_{13}. This approximate agreement may be evidence that in UBe_{13}, as in WBe_{13}, the screening of the field is actually caused by a light component with $m^* \approx m_0$. At this point we cannot draw more-detailed conclusions regarding the nature of the band structure of these systems or the mechanism for the pairing. We need both new experiments and a better understanding of the nature of heavy electrons themselves.

Some further information on the roles played by various groups of electrons and, possibly, various components of compounds comes from a study of the effect of impurities on the properties of these systems. The effect of substitution in the U or Be sublattice on the superconducting and normal properties of UBe_{13} was studied in Refs. 27 and 28. It was found that when U is replaced by an element with a similar electronic structure, e.g., Th or La, the temperature T_c decreases quite smoothly. The value $T_c = 0.4$ K was found for a Th impurity at a concentration $x = 0.05$. On the other hand, a substitution in the Be sublattice (with Cu or B) leads to an essentially complete suppression of the superconductivity (at $x \approx 0.05$, the value $T_c < 0.02$ K was found[28]). There are essentially no changes in the "heavy-fermion characteristics," in particular, the electron specific heat.

Doping of UBe_{13} with iron, and also neutron bombardment and hydrogen absorption lead to the same pronounced suppression of superconductivity.[25] The accompanying changes in the characteristics of the normal phase, in particular, the magnetic susceptibility, are quite slight. The reason for this behavior is not completely clear. This behavior may mean that it is the electrons of the wide bands, in particular, those genetically related to Be, which are playing an important role in establishing the long-range superconducting correlations in UBe_{13}, while the replacement of a central U atom—at which the heavy f electrons are localized—plays a minor role. However, we do not rule out the possibility that here we are simply dealing with a weaker scattering by isomorphic impurities such as Th and La.

4. NATURE OF THE SUPERCONDUCTING STATE

The experimental results which have attracted the greatest interest are those which show that the properties of $CeCu_2Si_2$, UBe_{13}, and UPt_3 at $T < T_c$ are quite different from the properties of ordinary superconductors with s-state pairing, which are described by the standard BCS theory. According to the theory, a gap Δ appears in the spectrum of elementary excitations at the Fermi surface below T_c, and

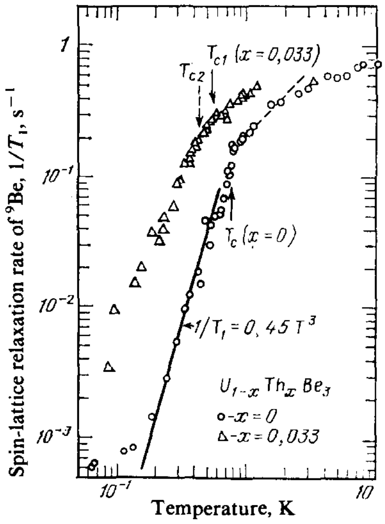

FIG. 2. Temperature dependence of the reciprocal of the spin-lattice relaxation time, $1/T_1$, of ^{9}Be nuclei in $U_{1-x}Th_xBe_{13}$ for $x = 0$ and $x = 0.033$ (Ref. 30). Solid line—Behavior $\sim T^3$ to $T > 0.2$ K; dashed line—Korringa law; solid arrows—T_c ($x = 0$) and T_{c1} ($x = 0.033$) in a field of 15.5 kOe; dashed arrow—T_{c2} for $x = 0.033$ and $H = 0$ for measurements of the specific heat.

such properties as the specific heat, the ultrasonic attenuation, and the nuclear-spin relaxation rate have an exponential temperature dependence. The disruption of this dependence in heavy-fermion superconductors is presently regarded in the literature as the basic indication of a possible nontrivial nature of the superconductivity in such systems.

It has been established, for example, that the specific heat of UBe_{13} is described approximately in the temperature interval $0.1T_c \leqslant T < T_c$ by the power law[9]

$$\frac{C_s(T)}{C_n(T_c)} \approx 2{,}8\left(\frac{T}{T_c}\right)^3.$$

In $CeCu_2Si_2$, various samples exhibit the behavior[2]

$$\frac{C_s(T)}{C_n(T)} \approx \left(\frac{T}{T_c}\right)^{\beta}, \quad \beta = 2{,}4-3.$$

The relaxation of the nuclear spin in the superconducting phase has been measured in [30]UBe_{13} and[31] $CeCu_2Si_2$. In UBe_{13}, the spin-lattice relaxation rate T/T_1 is described at $0.2 < T/T_c < 1$ by a T^3 law, while at $T < 0.2T_c$ it deviates from this law and has noticeably larger values (Fig. 2). In $CeCu_2Si_2$ in a zero field at $T \lesssim 0.3T_c$, the value of $1/T_1$ found by a nuclear-quadrupole-resonance method[31] becomes essentially constant or even increases slightly with decreasing temperature. In a field of 5.7 kOe, the behavior $1/T_1 \sim T^3$ is found down to 65 mK. These systems also lack the minimum in $1/T_1$ near T_c which is observed in ordinary superconductors.

Ultrasonic attenuation has been measured[32] in UPt_3. Again, a deviation from the ordinary exponential dependence was found; according to the data of Ref. 32, the results can be described well by $\alpha \sim T^2$ (Fig. 3).

All these results have served as arguments for the conclusion that the superconductivity in these systems is unusual. In particular, attempts have been made to explain these results by the suggestion[8-10] that the pairing in these systems does not occur in an s state but is instead anisotropic, e.g., of a p nature. For anisotropic pairing, the gap at the Fermi surface might vanish in certain directions. If this vanishing occurred at points, we would see at T^3 dependence for the specific heat, while if it vanished on lines we would see a T^2 dependence. The corresponding dependence for the ultrasonic attenuation would be T^4or T^2, and that for the spin relaxation would be T^5 or T^3. From the data on the ultrasonic attenuation and the nuclear magnetic resonance which we have already seen, we might conclude that the second of these possibilities prevails in these compounds, i.e., that the gap vanishes on lines of the Fermi surface, and that the quasiparticle state density is described by $N(E) \sim E$.

A detailed symmetry analysis of the possibilities which arise has been reported by Volovik and Gor'kov.[11] Similar ideas were expressed by Anderson.[12] The symmetry of the crystal must be taken into account in the analysis. For this reason, in contrast with a liqud, e.g., ^{3}He, it is not correct in this case to speak in terms of an s, p, or d pairing; it is necessary to classify the states which arise according to representations of the symmetry group of the crystal (with the complications which arise when the specific nature of the superconductivity is taken into account: gradient invariance, etc.). The detailed analysis[11] showed which types of symmetry of the order parameter are possible in principle, for which types the gap will remain over the entire Fermi surface, and for which it will vanish on lines or at points. There may be cases in which, in the presence of such zeros, the pairing will nevertheless be a singlet pairing (an analog would be d-wave pairing), and in principle there could be situations with a triplet pairing. With such nontrivial pairings many anomalous properties could be possible, some of which were discussed by Volovik and Gor'kov.[11] According to Volovik and Gor'kov,[11] lines of zeros could be seen only in the case of an anisotropic singlet pairing. Nevertheless, we do not yet have sufficient experimental information to make an unambiguous choice among the various possibilities. At this point we cannot even say with any confidence whether a nontrivial pairing actually occurs in these systems or whether the anomalous behavior outlined above has some other explanation. In particular, the nonexponential nature

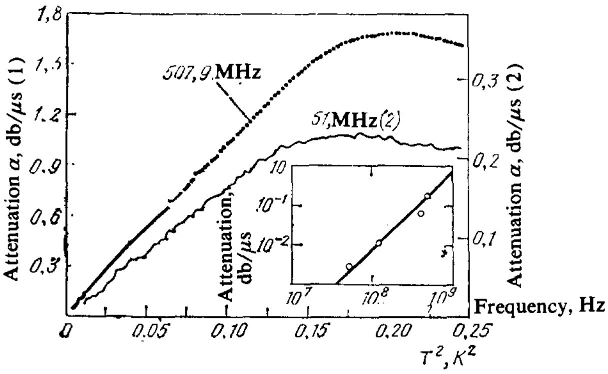

FIG. 3. Ultrasonic attenuation α in UPt_3 for two values of the frequency, as a function of T_2 (Ref. 32). The inset shows α as a function of the frequency; the solid line is the behavior $\sim\omega^2$.

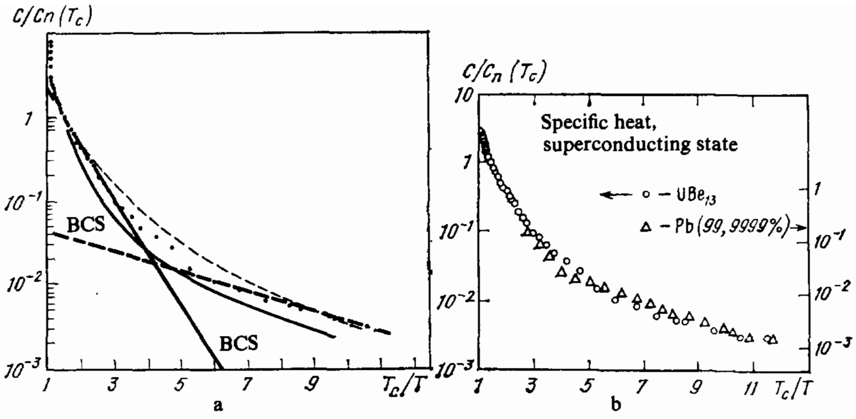

FIG. 4. a: Specific heat of UBe_{13} as a function of the temperature in the superconducting state according to the data of Ref. 6. Thin dashed line—Behavior in the case of p-type pairing as in the A phase of ^3He in the weakcoupling case; thin solid line—strong-coupling case; heavy solid and dashed lines—BCS theory for two gaps. b: Comparison of the superconducting specific heat of UBe_{13} with that of Pb (Ref. 34).

of the function $C(T)$ at $T < T_c$ might be interpreted (and has been, for niobium, for example[33]) as the result of the existence of two gaps Δ_i, for light and heavy groups of carriers (in niobium, these were gaps for s and d electrons) (Fig. 4a). The same effect might result from nothing more than an anisotropy of a gap, without a vanishing of the gap anywhere. Even for lead, a "classical" BCS superconductor, the behavior of $C(T)$ at $T < T_c$ in an appropriate scale corrsponds surprisingly well to the behavior of the specific heat in UBe_{13} (Fig. 4b; Ref. 34), which at one time served as the primary argument in favor of a nontrivial pairing in UBe_{13} (Ref. 9).

Volovik and Khmel'nitskiĭ[35] have offered an additional argument in favor of a nontrivial pairing. In a study of the specific heat in the $U_{1-x}Th_xBe_{13}$ system it was found[36] that at $0.02 < x < 0.04$ the superconducting transition splits in two, with nearly equal temperatures T_{c1} and T_{c2}. An NMR study gave no indication of the presence of any other transitions,[36] structural or magnetic, in this region; i.e., it could be assumed that these two transitions were transitions to different superconducting phases, differing in the nature (symmetry) of the order parameter. This interpretation, developed in Ref. 35, would actually be evidence that the pairing in UBe_{13} is of a nontrivial nature.[6)]

At the same time, there are arguments against an anomalous nature of the superconductivity in such systems. For example, an anisotropic pairing of this sort would have been manifested in a pronounced anisotropy of H_{c2} near T_c even in the cubic material[37] UBe_{13}. Experiments have yet to reveal any such anisotropy in UBe_{13} (Ref. 38), however.

In $CeCu_2Si_2$, the situation is not yet settled. Aliev *et al.*[50] discovered an anisotropy in the basal plane, but with a twofold rather than the expected fourfold axis. On the other hand, experiments by Onuki *et al.*,[51] apparently with high-quality $CeCu_2Si_2$ single crystals, revealed no corresponding anisotropy.

Yet another experiment capable in principle of providing some information on the type of pairing in heavy-fermion systems is a study of the Josephson effect. It has been suggested that if a pairing, in $CeCu_2Si_2$, say, occurs in a triplet state, then the Josephson effect would be suppressed in a contact with an ordinary *s*-type singlet superconductor. Experiments, on the other hand, have shown[39] that the ordinary Josephson effect occurs at a junction of $CeCu_2Si_2$ with Al. Steglich *et al.*[39] conclude from this result that the superconductivity itself in $CeCu_2Si_2$ is of the ordinary nature. On the other hand, a study of the Josephson effect for contacts of UPt_3 with Al, Nb, and UPt_3 has yielded negative results. Whether these results mean that the superconductivity in UPt_3 is anomalous is difficult to say at this point. There are many other, purely technological, factors which could lead to a negative result (in particular, we might note that the Josephson effect has also failed to appear at a UPt_3-UPt_3 contact, where the symmetry of the states on the two sides of the contact is identical). On the other hand, a theoretical analysis[58] shows that a Josephson tunneling between singlet and triplet superconductors is not forbidden. The spin-orbit interaction, combined with the inhomogeneity of the system near the contact, leads to a mixing of the singlet and triplet order parameters, making a Josephson effect possible. Nevertheless, there is still the possibility that the situations in different heavy-fermion compounds, discussed together above, are different, and that an ordinary singlet BCS pairing occurs in some of these compounds, e.g., $CeCu_2Si_2$, while an anisotropic pairing occurs in others.

If the pairing turns out to be of an ordinary nature, what possibilities are there for explaining the anomalous temperature dependence of various properties at $T < T_c$? One possibility is a possible strong pairing effect of "nearly magnetic" f centers, i.e., spin fluctuations. Magnetic impurities are known[40] to have a strong depairing effect on ordinary singlet superconductors, and in principle these impurities could set the stage for a gapless state in which there would of course be no exponential dependence for all properties below T_c. The effectiveness of the depairing influence of such impurities is characterized by the parameter

$$\lambda_m = c\frac{N(0)}{2T_{c0}}(g-1)^2 S(S+1)J^2,$$

where c is the concentration of magnetic impurities with spin S and g-factor g, and J is the exchange integral of their interaction with conduction electrons. A gapless state prevails for $0.91\lambda_{crit} < \lambda_m < \lambda_{crit}$. In the usual cases of impurities with a fixed moment, this region can be reached by varying the impurity concentration c. If we assume that the f centers are serving as depairing centers in our case, we have a slightly different situation. Their concentration is fixed in this case:

$c = 1$. On the other hand, by virtue of the Kondo effect, there is a progressive screening of the magnetic moment as the temperature is lowered. This effect is reflected in the behavior of the magnetic susceptibility (a transition from a Curie law to a Pauli susceptibility), and the anomalous temperature dependence of the resistance is frequently linked with this effect.[3,14] Correspondingly, as the temperature is lowered there will be a decrease in the factor $g^2S(S+1)J^2$ in the expression for λ_m, and λ_m itself will decrease. It might be suggested that in the absence of magnetic scattering the superconductivity would set in earlier, i.e., at a higher temperature. So far, however, we have not dropped to a temperature which is quite low in comparison with the Kondo temperature T_K (in such systems, we have $T_K \lesssim 10$ K); the depairing effect of this scattering is strong, $\lambda_m(T) > \lambda_{crit}$; and superconductivity does not set in. It is only after the temperature has become quite low (say $\sim 0.1T_K$) and the localized moments have become sufficiently screened that λ_m becomes smaller than λ_{crit}, and a superconductivity sets in.[7] In this picture, however, as the temperature is lowerd, and there is a corresponding continuous decrease in λ_m from $\lambda_m > \lambda_{crit}$ to $\lambda_m < \lambda_{crit}$, we would automatically go into a region of gapless superconductivity near T_c. Consequently, the behavior of various properties at $T \leqslant T_c$ which was observed experimentally could be explained by this approach. However, there is a real difficulty here: It is not clear whether the spectrum remains gapless as the temperature is lowered further, to $T \ll T_c$; it is also not clear whether it will be possible to obtain anything in the way of a regular (power-law) behavior at $T > T_c$. Admittedly, as we have already mentioned, this power-law behavior cannot always be seen clearly in experiments, and this behavior is generally disrupted at sufficiently low temperatures. In particular, in $CeCu_2Si_2$ the $C_s(T)$ dependence changes from $\sim T^2$ at $T \leqslant T_c$ to T^3 at lower temperatures.[29] In UPt_3 the specific heat turns out to be generally linear[29] $C_s(T) \sim T$, below T_c (at $\sim 0.5T_c < T < T_c$). This linear behavior would correspond to a true gapless situation. Below $\sim 0.5T_c$, however, $C_s(T)$ apparently begins to fall off much more sharply (this sharp decrease would be evidence of the appearance of a gap). This behavior would be consistent with the qualitative picture of depairing due to spin fluctuations which was drawn above (but we note that this picture is contradicted by data on the attenuation of ultrasound[32] in UPt_3, where a good $\alpha \sim T^2$ law is observed down to values $T \sim 0.1T_c$). The alternative possibility outlined above has not yet been subjected to thorough theoretical scrutiny.

In connection with the picture discussed above, we might also mention the materials in which superconductivity is induced by a magnetic field. The first such example was the compound[53] $Eu_{1-x}Sn_xMo_6S_8$. As the field H is increased, there is a succession of a superconducting phase, a normal phase, and then a superconducting phase again. This behavior has been attributed to the Jaccarino-Peter effect[54]: A compensation for the external magnetic field by the exchange field of localized Eu spins which are interacting in an antiferromagnetic fashion with conduction electrons. A similar effect has been observed in a heavy-fermion system,[52] $CePb_3$, but here the initial phase is not superconducting but antiferromagnetic. In this case, the compensation effect by itself cannot explain the observed behavior, and spin fluctuations appear to play a major role. Spin fluctuations make a negative contribution to the interelectron interaction constant[55] λ,

$$\lambda = \lambda_0 - A\chi, \quad A \sim J^2_{fd},$$

so that in weak fields λ turns out to be negative and magnetism "wins." As H is increased, on the other hand, the spin fluctuations (or the antiferromagnetic spin waves) are suppressed (χ decreases), and λ can become positive; i.e., the stage is set for the appearance of superconductivity.[55]

The same phenomenon can be seen in properties of "more ordinary" heavy-fermion superconductors. While the spin fluctuations in $CePb_3$ are strong enough to alter the nature of the ground state completely, they would lower T_c in systems of the UBe_{13} type according to this picture, but they would not destroy the superconductivity completely. The suppression of spin fluctuations by the magnetic field, on the other hand, which is used to explain the onset of superconductivity in $CePb_3$, would be responsible in UBe_{13} for the anomalous behavior of $H_{c2}(T)$ at low temperatures. According to the data of Ref. 56, H_{c2} increases essentially linearly with decreasing T, reaching a value $H_{c2}(0) \sim 90$ kOe, which is far above the paramagnetic limit. In this picture, this event could be explained on the basis that as the field is increased the suppression of spin fluctuations would cause the system to become, in a sense, a material with progressively larger values of T_c and thus H_{c2}. In principle, in materials of the UBe_{13} type there could also be a reentrant superconductivity; i.e., the superconductivity could reappear in strong fields.[57] In this connection it should be noted that the pronounced decrease in the resistance with the field (the decrease is by a factor of more than seven in a field $H \sim 150$ kOe) which is observed in UBe_{13} even at 1.7 K (Fig. 1) might be an indication that the superconductivity in UBe_{13} is actually a reentrant superconductivity. We wish to emphasize again that this picture would be possible in the case of a singlet pairing but not a triplet pairing.

There is yet another, admittedly indirect, argument in favor of a singlet superconductivity. An anomalous triplet pairing would be possible because of the contribution to the interelectron interaction of spin fluctuations, which are favorable for such a pairing.[10] In this case we might expect that the proximity of the system to magnetism (an increase in the magnetic susceptibility) would tend to promote superconductivity. Analysis of experimental data, on the other hand, leads to the opposite conclusion. A comparison of the susceptibility with the electron specific heat [the so-called Wilson ratio $R = \dfrac{\chi(0)}{\gamma}$] shows that this ratio increases[4] as we go from heavy-fermion superconducting systems ($CeCu_2Si_2$, UBe_{13}) to normal systems (nonmagnetic and nonsuperconducting) ($CeAl_3$, $CeCu_6$) and then to magnetic systems ($NbBe_{13}$, UCd_{11}, U_2Zn_{17}). In other words, it turns out that relatively small values of χ/γ are favorable for superconductivity. This observation is of course not a proof (it is not clear, for example, what role spin fluctuations would play for an anisotropic singlet pairing[11] of the d-wave pairing type), but it may serve as an argument against the frequently advanced, and overly direct, analogy with ^{3}He, with its triplet pairing.[9,10]

We have said essentially nothing about the attempts which are being made to analyze superconductivity theoretically in these systems at the microscopic level. The problem here is an inadequate understanding of just what heavy fermions are; only after this question is resolved will there be a solid basis for discussing superconductivity in such systems. Characteristically, the studies along this line have so far dealt for the most part with singlet superconductivity (see Ref. 42, for example). It is only just recently that we have begun to see papers[43,44] with first attempts to analyze other possibilities and to compare various types of pairing. These studies, however, deal with very simplified models, and it is unclear how their results relate to the experimental situation.

5. CONCLUSION

Heavy-fermion superconductors are clearly interesting systems. On the other hand, one must not be misled into believing that they constitute an absolutely isolated case among the large number of superconducting compounds which are known. As we have already pointed out, even among the compounds of U and Ce there are several whose characteristics vary smoothly from "normal" to "heavy-fermion." The prominent features of these systems which ultimately determine their anomalous properties—the strong interelectron correlation, the small effective band width, and the resulting proximity to a localized state—may also be seen, to some extent, in other systems, where, say, the band is narrow because of geometric or structural factors. Tendencies in this direction are seen, e.g., in cluster compounds. Chevrel phases[45] and ternary borides[46a] [in $PbMo_6S_8$, e.g., which is a superconductor which has not previously been classified as a heavy-fermion system, we find $\gamma \approx 100$ mJ/(mole·K^2) and $m^* = 11m_0$—apparently still the record high value for a material which does not contain 4f or 5f electrons].[46b]

Until now, superconductivity has usually been described on the basis of a free-electron model, and the actual crystal structure has not been very important. In the case of narrow bands, on the other hand, the crystal structure may play a fundamental role. As in the theory of the electron structure of solids, there are two approaches: the free-electron approximation and the strong-coupling approximation. The strong-coupling approximation is applicable in the case of narrow bands, and in the case of superconductivity we have apparently found entities for which a description of the strong-coupling type would be appropriate. In this case, even with an ordinary phonon attraction mechanism, and with pairing in a singlet state, the order parameter and the energy gap may carry information about the crystal structure and may be of the "strong-coupling" type, e.g., if $\Delta(k) = \Delta_0(\cos k_x + \cos k_y + \cos k_z)$ in a cubic crystal.[11,43,44] It is this type of anisotropic singlet pairing which now appears to be the leading candidate for describing the properties of heavy-fermion superconductors. Cluster compounds and perhaps certain other unusual new superconductors may also lie on the path to this other limiting case, exemplified best by heavy-fermion superconductors (although the absolute limit of narrow bands, in which the band width is smaller than the binding energy of the electrons in a Cooper pair, and the pairs can be regarded as truly localized,[47] does not occur even in such systems).

In summary, it can be said that extensive and varied material has been accumulated on the properties of heavy-fermion systems in both normal and superconducting phases. Many unique features of these systems, which qualify them as a genuinely special class of materials, have been found. It may be that in these systems we are seeing the first examples of nonstandard superconductors in which the pairing is anisotropic and possibly occurs in a triplet state. Although a more conventional interpretation of the observations is not ruled out, in any case the systems clearly deserve further experimental and theoretical study. Developments in this field are taking place extremely rapidly; by the time this brief review is published we will surely have seen some new results, and these new results may cast light on the fundamental questions involved here. We can only hope that the basic questions—the type of pairing—will have been resolved by the time this paper appears.

We wish to thank L. N. Bulaevskiĭ and L. P. Gor'kov for useful discussions.

1) The f level must nevertheless not be too far below ε_F, so that a magnetic ordering will not occur.

2) Correspondingly, the coefficient γ in the linear electron specific heat, $C = \gamma T$, depends on the temperature. In referring to the value of γ below, we mean the limit $\lim_{T\to\infty} \gamma(T)$ in all cases.

3) $CeAl_3$ does not become superconducting.

4) Everywhere below, γ is expressed in millijoules per mole per kelvin squared or, if the formula unit contains more than one f atom, in millijoules per mole per f atom per kelvin squared.

5) Lin *et al.*[52] have recently reported observing superconductivity in yet another compound of cerium with heavy fermions: $CePb_3$. The value of γ in that compound is certainly >200 and probably reaches ~ 1400 mJ/(mole·K^2). The superconductivity in $CePb_3$ is of a special nature, however: It arises only in strong magnetic fields, $\gtrsim 150$ kOe; in the absence of a field, $CePb_3$ is apparently an antiferromagnet with $T_N = 1.1$ K.

6) In recent experiments on ultrasonic attenuation in $U_{1-x}Th_xBe_{13}$, a peak was discovered at the lower transition point.[49] This peak was interpreted by the authors as evidence that the second transition is of a magnetic nature.

7) There are definite experimental indications of a relationship of this sort between superconductivity and the Kondo effect: Aliev *et al.*[41] have shown that the superconductivity which is induced by a magnetic field in $Ce_{1-x}La_xCu_2Si_2$ and $CeCu_2Si_2$ arises specifically upon an increase in T_K.

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Translated by Dave Parsons