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CHARACTERISTIC FEATURES OF THE EXOTIC SUPERCONDUCTORS:

A SUMMARY

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We summarize the results of a comprehensive examination of the characteristic features of the exotic superconductors, the superconductors so-labelled by Uemura and co-workers. In both the electronic and the crystal-chemistry properties, we find anomalous features which appear to be "universal" for these materials, as well as other features which are clearly not universal but common enough to be considered typical for these materials. Some implications of these anomalies are discussed.

Uemura and co-workers have shown that an unexpected phenomenological relation, $T_c \propto \lambda_L^{-2}$ (λ_L = London penetration depth), holds for many superconducting compounds [1]. They have labelled these materials "exotic", a term which has become widely accepted. Their list of such materials is now fairly extensive, and includes examples from the material families of cuprates, bismuthates, A_3C_{60} 's (A = alkali), Chevrels, A-15's, organics (1D & 2D), and heavy-fermions, together with $NbSe_2$, $LiTi_2O_4$, and several "almost heavy" relatives of the heavy-fermion materials: U_6Fe , UPd_2Al_3 , and U_2PtC_2 . These superconductors are strange in many respects, including their chemistry and crystal structures and their often-high T_c 's. It is notable that this collection includes *all* of the presently-known high- T_c superconductors, as well as a large fraction of what might be considered "novel superconductors". Careful study of their characteristic or typical features should therefore be worthwhile.

Phenomenological similarities among various subsets of these exotic materials have been noted by many investigators [2]. Although this is often with emphasis on similarities to the cuprate superconductors, such comparisons actually go back in time considerably before the discovery of cuprate superconductivity, and well before the work of Uemura *et al.* Typical and now well-known features which were identified in the earlier studies include strong to extreme type-II behavior, short coherence length, low charge-carrier density, very high resistivity, a narrow-band or large m^* aspect, insensitivity to a lattice of magnetic (local moment) rare-earth ions, and a tendency to low-dimensionality and/or clustering in the crystal structure. The heavy-fermion and cuprate examples have also focussed attention on the presence of a large Hubbard U interaction, and suggest that this may be a more common feature of the exotics.

With this background as motivation, we have undertaken a more comprehensive examination of the characteristic features of these exotic superconductors [3]. We found that some of the electronic features, which are anomalous from the standpoint of

conventional BCS and strong-coupling (Eliashberg) phenomenology, appear to be "universal" among the exotic materials. A number of other anomalous features are clearly *not* universal in this sense, but are nevertheless common enough to be considered typical for this class. Examination of the crystal chemistry likewise reveals some universal and also some typical but nonuniversal features. Detailed references for the following discussion can be found in Ref. 3.

The anomalous electronic features which appear to be universal for the exotic superconductors are: (a) strong-to-extreme type-II behavior ($\kappa \sim 10$ to 100), (b) low charge-carrier density (~ 1 per formula unit, or per active U site), (c) low-power-law (T^2 or T) resistivity near T_c , (d) very large resistivity at and above room temperature (large compared to lead, the strong-coupling prototype), (e) a region of upwards curvature in $H_{c2}(T)$, and (f) mass enhancement (reduced dispersion), as compared to band theory and the $(1+\lambda)$ enhancement factor from electron-phonon coupling. These properties have not all been verified for all of the exotic materials, but they are common enough (and without counterexamples) to suggest universality. They have sometimes been established for only a few or perhaps only one member of a material family, however, so that the applicability to the entire material family is an assumption.

Features which are clearly not universal, but nevertheless common enough to be considered typical, are: (g) unusually high T_c , (h) extremely short coherence length, (i) absence of a Hebel-Slichter (coherence) peak in $1/T_1$, (j) evidence for gap nodes, (k) an enlarged value of the gap ratio $2\Delta/k_B T_c$, (l) a "more square" form of $\Delta(T)$, *i.e.* a scaled form which lies above the familiar BCS form, (m) an anomalously large or small value of the specific heat ratio $\Delta C/\gamma T_c$, (n) insensitivity to a lattice of rare-earth ions with local moments, and (o) in several of the lower- T_c material families ($T_c < 12K$), a smooth maximum in the resistivity at a T about ten times T_c . (An extremely small isotope shift, $\alpha \sim$

0.05, is well known for the high- T_c cuprate YBCO, but this is not typical for the other exotics.) The anomalous electronic features for the individual materials or material families are summarized in Table 1.

In their crystal chemistry, a conspicuous feature for most of the exotic materials is the presence of very different types of ions, characterized by large electronegativity differences. There are usually some nonmetallic or semimetallic ions, which is counterintuitive for superconductivity, and sometimes there are very electropositive ions. Chemically speaking, we describe these as "strange formula" superconductors. Apparently because the heavy-fermion materials are characterized by a much smaller energy scale, however, their electronegativity differences can also be smaller, thus for these materials the disparate ions can consist entirely of metallic elements. With this caveat, the large electronegativity differences are a universal feature. A common but nonuniversal feature is the frequent occurrence of quasi-low-dimensionality (*e.g.* a layered structure) and/or clustering within the crystal structure. (The organic superconductors exhibit both reduced dimensionality and clustering simultaneously.) Large- U (Hubbard U interaction) units are obvious in the materials with isolated d or f ions: the cuprates, heavy-fermions, NbSe_2 , and LiTi_2O_4 . In other cases one can plausibly associate a large U with an ionic cluster or molecular unit, *e.g.* Mo_6 in the Chevrels, C_{60} in A_3C_{60} 's, organic molecule (or pair of molecules) in the organics. In the case of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO) a substantial U has been confirmed for the Bi 6s orbitals [4]. (The *chains* of d ions in the A-15's are admittedly problematic. We have offered a resolution for this case elsewhere [5].) Thus, the *plausibility* of a large- U unit seems to be a universal feature of the exotic superconductors.

This list of exotic features is representative but probably not exhaustive. We expect that further investigation will establish more of these features. (One such apparently common anomaly is a broad "mid-range" infrared absorption.) Using the present broad range of characteristic features, we have collected evidence to argue that the

superconducting borocarbides, short-chain analogs of the Chevrel compounds, and cubic Laves-phase cerium compounds are also exotic. Furthermore, we note that the majority of the many other known "strange formula" superconductors [6] also share the typical crystal chemistry features just described, so that these are also reasonable candidates to examine for exotic electronic features.

What can be deduced from this systematics? We mention some further observations and reasonable inferences, and then suggest an overall picture.

- (1) The typical T^2 resistivities indicate electron-electron or quasiparticle scattering, as has commonly been argued for the heavy-fermion materials. Furthermore, the observed T^2 coefficients are typically found to be near the Kadowaki-Woods line [7] for the valence-fluctuation and heavy-fermion materials. The $\rho \propto T$ behavior of the cuprates can also be explained by quasiparticle scattering, with the different power law being due to having the Fermi level close to the van Hove saddle-point energy in these materials [8].
- (2) The typical quasiparticle mass enhancement (beyond that attributable to electron-phonon coupling) is qualitatively consistent with a large U interaction.
- (3) Empirically, gap nodes are more likely to be found in materials with reduced dimensionality (*e.g.* planar compounds), but there is also evidence for strong (although nodeless) gap anisotropy in some cubic compounds (A-15's and A_3C_{60} 's). This and other evidence suggests an anisotropic-s-wave gap form (which does allow gap nodes) for the majority of these materials. (Here "s-wave" or "s-like" means that the gap has the full point-group symmetry of the lattice.) The other evidence just mentioned is from pairs of similar materials with and without gap nodes: hole-doped *vs.* electron-doped (and, recently, hole-overdoped) cuprates; ordered *vs.* disordered planar organics; YNi_2B_2C *vs.* $ThPt_2B_2C$. The heavy-fermion materials may be different, however, because of the more complex magnetic states of their uranium ions.
- (4) The similarities between the cuprates and the other exotic superconductors are quite extensive, as seen in Table 1, and the cuprates are therefore not as unique as is often

claimed. The possibility of the cuprates having highly anisotropic s-like pairing, with gap nodes, should therefore receive more serious consideration.

(5) The ratio ξ/a is quite interesting. This is the ratio of the coherence length ξ to a relevant (typically in-plane) lattice parameter a , or to the nearest-neighbor distance between U-bearing units if this distance is smaller. The *minimum* values of this ratio, within several of the exotic material families (cuprates, Chevrels, A_3C_{60} 's, organics), are only around 2.5 to 3.5, astonishingly small compared to the conventional values of $\sim 10^3$. This implies that the pairing must be distributed throughout much and possibly all of the Brillouin zone, instead of being concentrated near the Fermi surface.

(6) The smooth resistivity maximum which is found in some of the lower- T_c materials (especially the planar organics), is similar in form to that of several heavy-fermion materials. This has a natural explanation in terms of valence-fluctuation theory [9], which can also easily explain why the temperature of this maximum is typically about ten times T_c [5].

(7) The significance of the $T_c \propto \lambda_L^{-2}$ relation of Uemura and co-workers, their "universal relation", is not obvious. They have suggested that this is evidence of a "boson condensation" aspect for the superconducting transition, as in the $\xi/a \rightarrow 0$ limit of the BCS theory. But it has been shown that even the smallest known cases of ξ/a are not small enough to validate the simple boson-condensation picture [10]. (Recall also that in several cases a clear Fermi surface has been observed above T_c .) We think that this and the other evidence suggesting a boson picture [extensive upwards curvature in $H_{c2}(T)$, and a broad critical-fluctuation region] may be basically consistent with the BCS gap equation, with a pair interaction that induces pairing throughout the Brillouin zone. In any event, the correct interpretation of the Uemura relation must be consistent with the full range of the other anomalous features.

(8) Other investigators [11] have plotted the T_c 's of many of these materials against γ , the specific heat coefficient, but have not recognized any correlation which might correspond to the Uemura relation. (In contrast, however, a rough $T_c \propto \gamma^{-1}$ relation was recognized for several of these materials in Ref. 12.) The broad k -space distribution of pairing [comment (5)] is probably the reason why the correspondingly k -distributed quantity λ_L is more closely related to T_c than is the Fermi-surface quantity γ .

(9) Several kinds of evidence suggest a typical coexistence and synergism between the conventional phonon mechanism and some "new" but still s -wave-like mechanism, with different materials having different relative strengths of these mechanisms. This evidence includes the wide variability in ξ/a and the isotope shift (the latter being prominent for the cuprates), and the considerable deviations from a strict $T_c \propto \lambda_L^{-2}$ relation.

Portions of this phenomenology have often been used previously to argue support for various possible "new" pairing mechanisms. We find that this list of anomalous features is most consistent with a valence-fluctuation mechanism we have developed for the cuprates [13]. The match between the observed and the expected anomalies is remarkably extensive, and this applies even to the crystal chemistry features. Many of these anomalous electronic properties are exhibited by the cuprates (Table 1), and are at least qualitatively explained for the cuprates by this mechanism [13,5]. The crystal-chemistry features are seen here as *enabling features*, features which are necessary to justify a suitable Anderson-lattice model Hamiltonian and to provide an appropriate parameter regime. We have discussed this general picture previously [5], and a more thorough treatment is in preparation. We want to mention here that even the Uemura relation can be qualitatively understood within this picture. The reasoning is outlined in the schematic relations

$$\lambda_L^{-2} \propto n_s/m^* \sim 1/m^* \propto T_K > 10 T_c, \quad (1)$$

where T_K is a Kondo temperature (here identified with a resistivity maximum, if this exists). The main arguments for a valence-fluctuation picture were presented in Ref. 13, and are reinforced by (a) the resistivity maximum in a number of low- T_c examples, and its typical $T(\rho_{\max}) \sim 10 T_c$ relation, and (b) the present Eq. 1. The Eq. 1 connection is also supported by an early paper comparing the cuprate and heavy-fermion superconductors [12].

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TABLE CAPTION

Table 1. Anomalous Electronic Properties of the Exotic Superconductors

A “+” or “-” indicates reasonably good evidence that the feature does or does not occur. In many cases the evidence is available for only one or a few members of a material family.

See Ref. 3 for details.

Table 1. Anomalous Electronic Properties of the Exotic Superconductors

	cuprates	bismuthates	A ₃ C ₆₀ 's	A-15's	Chevels	organics	heavy-fermions	U ₆ Fe	NbSe ₂	LiTi ₂ O ₄	borocarbides	short-chain Chevrels	C-15 ceriums
strong type-II superconductivity	+	+	+	+	+	+	+	+	+	+	+	+	+
extremely small ξ/a	+		+		+	+							
upwards curvature in $H_{c2}(T)$	+	+	+	+	+			+	+	+	+		+
large and low-power-law resistivity	+	+	+	+	+	+	+	+			+		+
maximum in resistivity (of moment-unbinding form)	-	-	-	-	-	+	+	-	+		-	+	-
low charge-carrier density	+	+	+		+	+			+	+		+	
m^* or state-density enhancement (beyond band and el-ph value)	+		+	+	+	+	+			+	+		
small isotope effect	+					+							
insensitivity to lattice of rare-earth local moments	+				+						+		
anomalous gap and/or specific-heat ratio	+		+	+			+				+		+
"more square" $\Delta(T)$ form	+	-	+			+				-	-		
absence of Hebel-Slichter peak	+		-	-	-	+	+	-			+		
evidence for gap nodes	+					+	+				+		
effective structure dimensionality	2	3	3	3	3	2 ^{or} 3	3 ^{or} 2		2	3	2	3 ^{or} 2	3

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