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CHARACTERISTIC FEATURES OF THE EXOTIC SUPERCONDUCTORS:
EVIDENCE FOR A COMMON PAIRING MECHANISM

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We report on a comprehensive examination of the exotic superconductors (the materials so-labelled by Uemura and co-workers), to determine as far as possible the true systematics among their many anomalous features. In the crystal-chemistry aspects as well as in the electronic properties, we find features which appear to be universal for these materials, and also features which are clearly not universal but which are common enough to be considered typical for these materials. A number of implications are presented. It appears that all of these materials are sharing some "new" pairing mechanism, usually in addition to the conventional phonon mechanism.

Soon after the discovery of cuprate superconductivity, as data revealed a number of anomalies in the electronic properties, anomalies from the standpoint of conventional BCS and strong-coupling Eliashberg phenomenology, phenomenological similarities to various other unusual superconductors were noted by many investigators. There turned out to be considerable overlap between these observations and various earlier recognitions of similarities among unusual non-cuprate superconductors.¹ One could therefore reasonably suspect that the cuprates are merely one family in a much wider class of materials which are sharing some "new" pairing mechanism (usually in addition to the conventional phonon mechanism). This tantalizing but rather vague line of enquiry was later offered a dramatic focus by the work of Uemura and co-workers.² They demonstrated that many superconductors follow a quite unexpected relation, $T_c \propto \lambda_L^{-2}$, where λ_L is the $T \rightarrow 0$ London penetration depth. Uemura *et al.* have called these materials "exotic superconductors", a term which has now gained wide acceptance. Their list of exotic materials is quite interesting. This includes examples from the families of cuprates, bismuthates without copper (BKBO), alkali fullerenes, Chevrels, A-15's, organics (1D & 2D), and heavy-fermions, together with NbSe₂ and LiTi₂O₄ (the first high- T_c oxide), and several "almost heavy" relatives of the heavy-fermions: U₆Fe, UPd₂Al₃, URu₂Si₂, and U₂PtC₂. It is striking that this list includes all of the known high- T_c superconductors, as well as many other novel materials that are or have been of great interest in basic superconductivity research. Typical and now well-known features which were identified in the earlier studies¹ 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. These aspects, and the surprising

systematics of Uemura *et al.*, strongly suggest that more careful study of these materials could yield still further systematics and useful insights, and thus provide further guidance for theory.

With this background as motivation, we have pursued this program in a thorough and comprehensive manner. We have examined and compared the data for each one of the exotic materials, to try to find the true systematics among their anomalous features. (We only consider anomalies which are found in several cases, so that a trend can be argued.) The results, as well as the historical background, are in a report which we hereafter call R.³ Here we shall summarize these results, provide some comments, and present some implications which can be deduced with reasonable confidence, independent of a specific theory. We have found that some of the electronic features 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 aspects likewise reveals some universal and also some typical but nonuniversal features. References and many further details can be found in R.

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-bearing 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 prototype strong-coupling superconductor), (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 ($T_c < 12\text{K}$), a smooth maximum in the resistivity at a T about ten times T_c . (An extremely small isotope shift, $\alpha < 0.05$, is well known for the high- T_c cuprate YBCO, but this is *not* typical for the other exotics.)

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. We have therefore described these materials chemically as "strange-formula superconductors".³ 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 a number of 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 probably not exhaustive. We expect that further investigation will establish more of these features, as well as refining some of the present ones. [Another apparently common anomaly is a broad "mid-range" infrared absorption. Also, the experimental identification of $H_{c2}(T)$ is still problematical.] Using the present broad range of characteristic features, we have collected evidence to argue that the superconducting borocarbides, the short-chain analogs of the Chevrel compounds, and the cubic Laves-phase cerium compounds are also exotic. Furthermore, we note that the majority of the many other known "strange formula" superconductors⁶ 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 offer 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 line⁷ 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), consistent with a general argument in R (Sec. 3.3). 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.)

(4) The other evidence just mentioned for a general anisotropic but s-like gap form is from pairs of similar materials with and without gap nodes: hole-doped vs. electron-doped cuprates, $\text{YNi}_2\text{B}_2\text{C}$ vs. $\text{ThPt}_2\text{B}_2\text{C}$, and apparently also an ordered vs. a disordered planar organic. The underlying argument here is that for an s-like gap form the removal of gap nodes can be achieved very simply, either by modifying basic electronic parameters to reduce the gap anisotropy, or by an effective angle-averaging due to dirt or other disorder. (In contrast, for a d-wave or other $\ell \neq 0$ gap form an elimination or avoidance of gap nodes is typically attributed to a violation of time-reversal invariance.) The uranium heavy-fermion materials are apparently different, however, probably because of the more complex magnetic states of their uranium ions. (This may also be the case for Sr_2RuO_4 .)

(5) The similarities between the cuprates and the other exotic superconductors are quite extensive, in spite of their also having some apparently unique features [stripes and a pseudogap; see point (1) about the linear resistivity]. The cuprates are certainly not as unique as is often claimed. The present overall systematics should therefore be very relevant for the quest to understand cuprate superconductivity. One consequence is that the possibility of the cuprates having highly anisotropic s-like pairing, with gap nodes, should receive more serious consideration.⁹

(6) 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.

(7) 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,¹⁰ which can also easily explain why the temperature of this maximum is typically about ten times T_c .⁵

(8) 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 (or rather of $k_F \xi$) are not small enough to validate the simple boson-condensation picture.¹¹ (Recall also that in several cases a clear Fermi surface has been observed above T_c . For cuprates there is also strong evidence against this boson picture from specific-heat data.¹²) 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, provided there is 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.

(9) Other investigators¹³ 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. 14. This appears as only a very rough and indefinite trend in the first paper of Ref. 13, ignoring the elemental superconductors in this plot.) The broad k -space distribution of pairing [comment (6)] 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 .

(10) 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. Although our aim throughout this phenomenological study has been to let the data speak for itself, it is appropriate to mention our theoretical bias. We believe that this list of anomalous features is most consistent with a valence-fluctuation mechanism we have developed for the cuprates.¹⁵ 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, and are at least qualitatively explained for the cuprates by this mechanism.^{15,5} The crystal-chemistry features are seen here as *enabling features*, features which are necessary to justify an Anderson-lattice type of model Hamiltonian and to provide an appropriate parameter regime. We have discussed this general picture previously⁵ and have briefly outlined this at the end of R; a more thorough treatment will appear elsewhere.¹⁶ 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

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

where T_K is a Kondo temperature (here identified with a resistivity maximum, if this exists), and where the last of these relations is explained in Refs. 10 and 5. The main arguments for

a valence-fluctuation picture were presented in Ref. 15, 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.¹⁴

In conclusion, we want to emphasize that (a) the very extensive similarities, in crystal chemistry as well as in electronic properties, strongly suggest that this entire class of materials is sharing some "new" pairing mechanism, usually in addition to the conventional phonon mechanism, and (b) the cuprates are similar in many ways to the other exotics. This overall systematics should therefore be very relevant for the understanding of cuprate superconductivity.

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