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# Phenomenological trends for heavy Fermi liquids and narrow-band metals

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A phenomenological correlation is presented for the magnetic susceptibility $\chi^*$ and the electronic heat-capacity coefficient $\gamma^*$ of a large number of narrow-band and heavy-fermion metals. A novel method of plotting $\chi^*/\gamma^*$ vs $\gamma^*$ reveals quantitative boundaries for distinct regions of superconducting, magnetically ordered, and paramagnetic ground states. It is suggested that magnetic interactions are a primary limitation for the $T_c$ of "conventional" superconductors, whereas a more delicate interplay exists between magnetic order, paramagnetism, and superconductivity above a threshold value of $\gamma^*$ which defines the onset of magnetic order.

The recent identification of the related "Kondo-lattice," "valence-fluctuation," and "heavy-fermion" solids has presented new challenges to the theory of nearly localized electron states in metals.[1-3] Substantial theoretical progress has been made toward solving the difficult problem of treating the delocalization of impurity *d*- or *f*-electron "core" states due to hybridization with conduction-electron levels in metals.[4] However, there is currently no quantitative model for a *lattice* of nearly localized electrons, as more difficult technical problems have been encountered.[5] Fortunately, it presently seems almost certain that the lowest-lying states of these strongly interacting systems can still be described in terms of Landau Fermi-liquid theory.[6]

Landau theory includes, in principle, all interactions within a Fermi liquid and is able to set down parametric relationships between various observables, such as magnetic susceptibility and heat capacity.[7] Unfortunately, present-day many-body theory cannot quantitatively treat all of the myriad interactions present in a real metal. Therefore, the extreme generality of Landau's theory in the end usually reduces it to a phenomenological treatment of experimental data. Discussions of various Fermi-liquid parameters are extremely common in the current literature concerning heavy-fermion and mixed-valence materials.[2,3,8] However, these parameters are usually only taken as a rough guide to the underlying physics of a given material, and some severe problems appear to exist in using this approach for a quantitative comparison with microscopic models.[8] Nevertheless, there is a need for identifying experimental trends which will indicate the quantitative significance of various Landau parameters and provide clues concerning the microscopic interactions present in complex Fermi liquids.

A comprehensive discussion of the many Landau parameters is beyond our expertise. Instead, we will focus on the magnetic susceptibility $\chi^*$ and the coefficient of electronic heat capacity $\gamma^*$. A summary of the relevant experimental results[9] for a large number of transition-metal, Yb, Ce, Sm, U, Np, and Pu compounds is given in Fig. 1, which consists of a plot of an "enhancement ratio" $R$ vs $\gamma^*$, where $R$ is defined by[8]

$$R = \lim_{\substack{T\to 0 \\ \text{or } T\to T_c^+}} \frac{1}{3}\left(\frac{\pi k_B}{\mu_B}\right)^2 \frac{\chi^* T}{C_{el}^*} . \quad (1)$$

Note that $\chi^*$ is the total (enhanced and uncorrected[10]) magnetic susceptibility, $C_{el}^*$ is the enhanced electronic contribution to the heat capacity, and the value of $R$ is evaluated at the lowest possible temperature above the onset of any cooperative phase transition (at $T_c$).

The plot, as hoped, reveals some rather striking trends:

(1) Magnetic order is observed only for $\gamma^* \gtrsim \gamma_M^* = 4\times10^4$ erg/cm$^3$ K$^2$. There are no superconductors observed in the subregion of magnetic order defined by $\gamma_M^* \lesssim \gamma^* \lesssim 10^5$ erg/cm$^3$ K$^2$.

(2) A small cluster of heavy-fermion superconductors ($CeCu_2Si_2$, $UPt_3$, $UBe_{13}$) occurs near $\gamma^* \sim 1\times10^5$ erg/

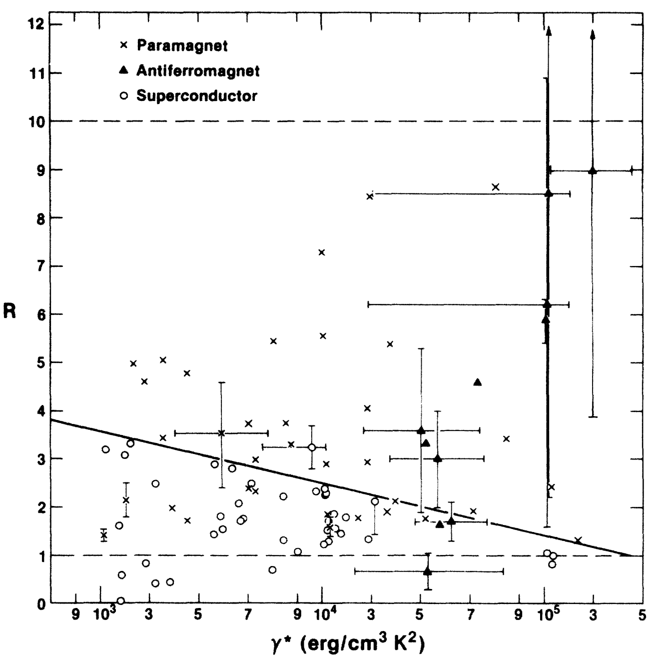


FIG. 1. Enhancement ratio $R$ vs electronic heat-capacity coefficient $\gamma^*$ for various $A$15-, $AuCu_3$-, NaCl-type transition-metal compounds, noble transition elements, Ce, U, Yb, and Np compounds, SmS (high pressure), and $PuBe_{13}$. Note the quasilogarithmic abscissa. The two horizontal broken lines denote the range of exchange enhancement $S$ expected from recent Fermi-liquid models (Refs. 12 and 13). The solid diagonal line denotes the critical value $R_c$ above which superconductivity does not generally occur. Error bars reflect difficulties in accurately estimating $\gamma^*$ for certain antiferromagnets or sample dependence of $R$ and $\gamma^*$. Note that elemental Cu has $\gamma^* \sim 0.7$ mJ/mole K$^2$ → $\sim 1\times10^3$ erg/cm$^3$ K$^2$.

 

$cm^3 K^2$ and $R \sim 1$, and this cluster is well isolated from other superconductors by the region of magnetic order.

(3) Essentially all of the superconducting materials examined fall below a diagonal line shown in Fig. 1, indicating a critical value $R_c(\gamma^*)$ above which superconductivity cannot occur.

(4) Nearly all of the materials examined exhibit $1 \lesssim R \lesssim 10$, consistent with the predictions of recent Fermi-liquid theories.[11-13]

(5) Paramagnetic materials appear to occur almost everywhere in the $R$-$\gamma^*$ plane, although there are notable vacant regions. Each one of these observations deserves further discussion.

The occurrence of antiferromagnetism only for $\gamma^* \gtrsim \gamma_M^*$ is a remarkable feature of Fig. 1, and has been hinted at in a previous discussion of a few heavy-fermion U materials.[14] We have also analyzed heat-capacity and susceptibility data for a number of additional compounds which could not be easily included in Fig. 1. These data are summarized in Table I which includes ferromagnets (for which $R \rightarrow \infty$ at the ordering temperature $T_M$) and certain antiferromagnets for which $\gamma^*$ could not be accurately estimated near $T_M$. These results lead us to conclude that $\gamma_M^*$ is a heretofore unrecognized threshold for *general* types of magnetic order for a variety of metallic solids.

The complete isolation of the small sector of heavy-fermion superconductors ($CeCu_2Si_2$, $UBe_{13}$, and $UPt_3$) by a surrounding region of magnetic order is a novel and striking demonstration of the unique nature of these materials. The unusual sensitivity of the magnetic and superconducting properties of heavy-fermion materials to impurities[15] and their singular position in Fig. 1 suggest that an extremely delicate balance exists between these two ground states, if not a common mechanism.

The nonoccurrence of superconductivity for $R > R_c(\gamma^*)$ evidently persists across the entire range of $\gamma^*$ shown in Fig. 1, and implies that this defines a region of exchange-enhanced paramagnetism. This is a striking illustration of the inverse correlation between the superconducting $T_c$ and $R$ already noted.[8] Also noteworthy is the presence of several high-$T_c$ superconductors ($Nb_3Sn$, $Nb_3Al$, $V_3Ga$, $V_3Si$, etc.) at $\gamma^* \gtrsim 1 \times 10^4$ erg/cm$^3$ K$^2$, just below the threshold $\gamma_M^*$ for magnetic order. The bounding of a large number of different superconductors by $R_c$ and $\gamma_M^*$ strongly suggests that magnetism is more important in limiting $T_c$ than lattice instabilities.[16,17] The present empirical definitions of $R_c$ and $\gamma_M^*$ constitute, to our knowledge, the first identification of quantitative limits imposed by magnetism on superconductivity.

We now address the practical and theoretical implications of these observations. The universal correlation of the heat-capacity behavior with the occurrence of superconducting and magnetically ordered ground states can be related to the lattice and electronic energy scales which are derivable from calorimetric data. The onset of magnetic order at $\gamma_M^*$ is generally characterized by the Fermi temperature $T_F^* \gtrsim \Theta_D$, where $\Theta_D \sim 100$–$400$ K is the Debye temperature of a typical rare-earth or actinide compound, and $T_F^* = \pi^2 k_B \rho / 2\gamma^*$, where $\rho$ is the fermion density.[18] This results in a situation where the Fermi velocity is of the same order as the sound velocity. Therefore, the interaction between the heavy-fermion quasiparticles and the lattice is highly nonadiabatic, and some of the standard assumptions of many-body theory break down.[5]

Anderson has pointed out[19] that $\Theta_D$ and $T_F^*$ define cutoff energies for the electron-phonon and Coulomb interactions, respectively, and that the nature of the superconducting pairing will be crucially dependent on the relative sizes of these scales. Bedell and Quader[13] have suggested that when $T_F^* \gtrsim \Theta_D$, competitive (electron-phonon) singlet and (paramagnon) triplet pairing interactions will suppress one another, leaving the door open to magnetic order. On the other hand, when $T_F^* < \Theta_D$, non-BCS superconducting interactions are favored in a more stringent competition with magnetic correlations.[11-13,19,20] The experimental trends given in Fig. 1 and Table I are indeed consistent with these notions, given the extended region of nonsuperconductivity between the heavy-fermion superconductors for which $T_F^* < \Theta_D$ (i.e., for $\gamma^* \sim 10^5$ erg/cm$^3$ K$^2$) and the lighter-mass superconductors for which $\Theta_D \ll T_F^*$ (where $\gamma^* < \gamma_M^*$). Other model calculations by Kim[16] point out that the electron-phonon interaction may become "exchange-enhanced" in low-$T_F^*$ materials and lead to an interplay between singlet superconductivity, magnetic order, and lattice instabilities, consistent with the observed proximity of high-$T_c$ superconductors to $\gamma_M^*$.

It is particularly remarkable that such a large number of transition-metal, Ce, U, and Np compounds lie in the region $1 \lesssim R \lesssim 5$, since the definition [Eq. (1)] of $R$ does not consider spin-order coupling, crystalline-electric-field (CEF)

TABLE I. Additional compounds exhibiting magnetic order. Ranges of parameters reflect either sample irreproducibilities or difficulties in accurately estimating $\gamma^*$ near the ordering temperature. Data are taken from the literature. The two types of order are antiferromagnetic (AFM) and ferromagnetic (FM).

| Compound | $\gamma^*$ ($10^4$ erg/cm$^3$ K$^2$) | $R$ | $T_M$ (K) | Type of order |
|---|---|---|---|---|
| TmS | 35 | 20 | 5.2 | AFM |
| $CeCu_2$ | 13–46 | 3.9–14 | 3.5 | AFM |
| $CePt_2$ | 8.6–100 | 3.4–41 | 1.6 | AFM |
| CePt | 5.2–12 | ··· | 5.8 | FM |
| $NpOs_2$ | 2.9–5.3 | ··· | 7.5 | FM |
| $CeAl_2$ | 3.6–110 | 1.0–22 | 3.8 | AFM |
| $CeGe_2$ | 3.4–3.9 | ··· | 7 | FM |
| UPt | 2.8–4.3 | ··· | 30 | FM |
| $Yb_3Pd_4$ | 1.3–26 | 32–64 | 3 | AFM |

effects or band-orbital magnetism; i.e., it is a spin-$\frac{1}{2}$ ratio.[18] We therefore propose $R$ only as an indirect measure of the exchange enhancement $S$. Nevertheless, the general occurrence of low values of $R$ strongly supports the "nearly localized" or "Brinkman-Rice" model of heavy Fermi liquids which predicts $R \lesssim 10$,[11-13] as opposed to the early paramagnon models in which $R$ was unbounded.[21]

On the other hand, there are several paramagnetic Yb compounds (YbCuAl, $YbCu_2Si_2$, $YbAl_3$) which exhibit $R \sim 8$, and the antiferromagnets TmS and $Yb_3Pd_4$ which exhibit $R \sim 20$ and $R \gtrsim 32$, respectively, in clear distinction from the general trends established for Ce, U, and Np compounds. We interpret this as an indication that spin-orbit and CEF interactions may have to be taken into account in calculating $S$ from these data.[22] A more detailed analysis suggests that the $R$ values for Ce and Yb compounds shown in Fig. 1 can be quantitatively understood within an alternate approach which includes CEF effects.[23] Unfortunately, we currently know of no analogous model which may be applied in the case of U materials. Further, the increasing occurrence of $R < 1$ for $\gamma^* << 10^4$ erg/cm$^3$K$^2$ signals the increasing relative importance of orbital and band-structure effects such as Landau-Peierls diamagnetism as the density of states decreases toward typical transition-metal values.[8] Our results demonstrate that more extensive data and quantitative models for Eu, Tm, Sm, U, Pu, and Np materials are highly desirable in order to achieve a more detailed relationship between $R$ and $S$ and the occurrence of superconductivity and magnetism.

The $R$-$\gamma^*$ correlation is a very useful guide in evaluating data and suggesting new directions for research. For example, $Yb_3Pd_4$ (see Table I), $CeCo_2$ ($\gamma^* \sim 9.5\times10^3$ erg/cm$^3$K$^2$, $R \sim 3.3$) and $NpSn_3$ ($\gamma^* \sim 5.3\times10^4$ erg/cm$^3$K$^2$, $R \sim 0.7$) appear to have anomalous values of $R$. This could indicate that these compounds are particularly interesting candidates for further study. Alternatively, anomalously large values of $R$ and sample dependence of the $\chi^*$ and $\gamma^*$ data (as observed for $CeCo_2$) may indicate that magnetic impurity phases are present and influence experimental results.

$URu_2Si_2$ has recently been reported to be the first example of the simultaneous occurrence of heavy-fermion superconductivity ($T_c \lesssim 1.4$ K) and antiferromagnetic order ($T_M = 17.5$ K).[24] The $R$-$\gamma^*$ correlation is remarkably consistent with the behavior of this material in the *two distinct* Fermi-liquid phases defined above [$\gamma^* \sim (3.1-3.7)\times10^4$ erg/cm$^3$K$^2$, $R \sim 1.6$] and below [$\gamma^* \sim (1.0-1.4)\times10^4$ erg/cm$^3$K$^2$, $R \sim 3.5$] $T_M = 17.5$ K. Although there is, as yet, no direct corroboration of magnetic order from neutron diffraction experiments, the proximity of $URu_2Si_2$ to the magnetic threshold $\gamma_M^*$ is consistent with a situation in which superconductivity and magnetic order are of comparable stability.

Isolated aspects of the trends discussed herein have been touched upon by several authors from various points of view.[3,8,14,25-27] However, the utility of plotting $R$ vs $\gamma^*$ has heretofore gone unappreciated. This type of correlation leads to many interesting speculations and supports certain new theoretical ideas. It is hoped that other workers will regularly evaluate experimental results with an eye toward improving the quantitative details of the $R$-$\gamma^*$ plot introduced here.

In summary, we find that the occurrence of superconductivity and magnetic order are delineated by three parameters. $R_c(\gamma^*)$ defines a critical value of effective exchange enhancement which limits superconductivity. The comparative values of $T_F^*(\gamma^*,\rho)$ and $\Theta_D$ define at least three types of ordered ground states. "Conventional" superconductivity occurs in an adiabatic regime where $T_F^* >> \Theta_D$. Magnetic order commences in a nonadiabatic regime where $T_F^* < \Theta_D$. "Heavy-fermion" superconductivity and magnetic order occur for $T_F^* < \Theta_D$.

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