



## New correlated electron physics from new materials

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### A B S T R A C T

Many important advances in the physics of strongly correlated electron systems have been driven by the development of new materials: for instance the filled skutterudites  $MT_4X_{12}$  ( $M$  = alkali metal, alkaline earth, lanthanide, or actinide;  $T$  = Fe, Ru, or Os;  $X$  = P, As, or Sb), certain lanthanide and actinide intermetallic compounds such as  $URu_{2-x}Re_xSi_2$  and  $CeTIn_5$  ( $T$  = Co, Rh, or Ir), and layered oxypnictides and related materials. These types of complex multinary d- and f-electron compounds have proven to be a vast reservoir of novel strongly correlated electron ground states and phenomena. In these materials, the occurrence of such a wide range of ground states and phenomena arises from a delicate interplay between competing interactions that can be tuned by partial or complete substitution of one element for another, as well as the application of pressure, and magnetic fields, resulting in rich and complex electronic phase diagrams in the hyperspace of temperature, chemical composition, pressure and magnetic field. It seems clear that this type of “materials driven physics” will continue to play a central role in the development of the field of strongly correlated electron systems in the future, through the discovery of new materials that exhibit unexpected phenomena and experiments on known materials in an effort to optimize their physical properties and test relevant theories.

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### 1. Introduction

This paper is based on a contribution by the first author to a special plenary session on “New Trends in Correlated Electron Physics” at SCES 2008 that was shared with two other speakers, Professors Flouquet and Onuki. The theme of this contribution was the crucial role developments in novel materials have played in the advancement of the physics of correlated electron materials. A number of examples illustrating this theme were discussed in the special plenary talk, some of which are briefly described in this paper. Several of these examples are drawn from the work of the first author and his research group and collaborators. Due to space limitations, it was not possible to include a comprehensive list of references; we have therefore cited relevant review articles, where possible, which contain references to the original work.

During the past half-century, many of the advances in the physics of correlated electron materials have been driven by developments

in materials (“materials driven physics”). In Table 1, we list some of the areas of research that have emerged during this period and the materials that led to these advances. This is a partial list that is based on the principal interests of our research group over the years. Many of the materials that have been responsible for the more recent advances are multinary (consisting of two or more elements) transition metal, rare earth, and actinide compounds in which the localized d- and f-electron states are hybridized with conduction electron states. These materials generally have crystal structures that consist of complex arrangements of several different types of atoms, resulting in large unit cells, molecular units or “clusters,” atomic layers, low-dimensionality, lack of inversion symmetry, etc. Competing interactions, based on coupled charge, spin, orbital, and lattice degrees of freedom, can be readily tuned by varying control parameters such as chemical composition ( $x$ ), pressure ( $P$ ), and magnetic field ( $H$ ), yielding a wide variety of correlated electron phenomena and rich and complex phase diagrams in the hyperspace of  $x$ ,  $T$ ,  $P$ ,  $H$ , etc. Two situations are illustrated by the examples considered in the following sections: (1) one interaction survives at the expense of the others to produce a known phenomenon and (2) several interactions conspire to produce an entirely new phenomenon.

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**Table 1**

Listed are some of the areas of research that have emerged during the past half-century and the materials that led to these advances.

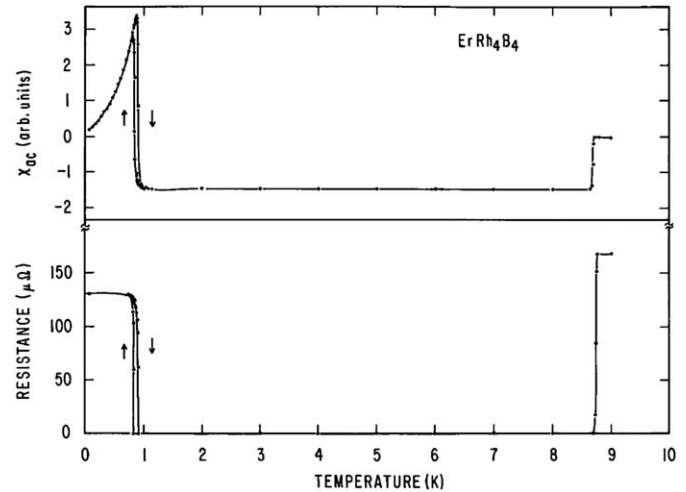
Material	Research problem
ZrZn <sub>2</sub> , Sc <sub>3</sub> In	Weak ferromagnetism
LnMo <sub>6</sub> X <sub>8</sub> (X = S, Se)	Magnetically ordered superconductors
LnRh <sub>4</sub> B <sub>4</sub> , LnRh <sub>x</sub> Sn <sub>y</sub> , LnNi <sub>2</sub> B <sub>2</sub> C	<ul style="list-style-type: none"> <li>• Coexistence of superconductivity and antiferromagnetism</li> <li>• Re-entrant superconductivity due to onset of ferromagnetism</li> <li>• Sinusoidally modulated magnetic state that coexists with superconductivity</li> </ul>
La <sub>1-x</sub> Ce <sub>x</sub> , La <sub>1-x</sub> Ce <sub>x</sub> Al <sub>2</sub> , (La <sub>1-y</sub> Th <sub>y</sub> ) <sub>1-x</sub> Ce <sub>x</sub>	Kondo effect in superconductors <ul style="list-style-type: none"> <li>• Re-entrant superconductivity due to Kondo effect</li> </ul>
La <sub>2-x</sub> M <sub>x</sub> CuO (M = Ba, Sr, Ca, Na)	High temperature superconductors
R <sub>2-x</sub> M <sub>x</sub> CuO <sub>4-y</sub> (Ln = La, Pr, Nd, Sm, Eu; M = Ce, Th)	(after 1986)
LnBa <sub>2</sub> Cu <sub>3</sub> O <sub>7-d</sub> , Bi <sub>2</sub> Sr <sub>2</sub> Ca <sub>n-1</sub> Cu <sub>n</sub> O <sub>2n+4</sub> , Tl <sub>2</sub> Ba <sub>2</sub> Ca <sub>n-1</sub> Cu <sub>n</sub> O <sub>2n+4</sub> , Hg <sub>2</sub> Ba <sub>2</sub> Ca <sub>n-1</sub> Cu <sub>n</sub> O <sub>2n+4</sub>	High temperature superconductors (before 1986)
V <sub>3</sub> Si, Nb <sub>3</sub> Sn, Nb <sub>3</sub> Al, Nb <sub>3</sub> Ge	Valence fluctuations in lanthanide compounds
Ce metal, SmS (gold phase), SmB <sub>6</sub>	Heavy fermion metal (magnetic origin)
CeAl <sub>3</sub>	Heavy fermion superconductors (magnetic origin)
CeCu <sub>2</sub> Si <sub>2</sub> , UBe <sub>13</sub> , UPt <sub>3</sub>	Heavy fermion metal (electric quadrupole origin)
PrInAg <sub>2</sub> , PrFe <sub>4</sub> P <sub>12</sub>	Heavy fermion superconductors (electric quadrupole origin)
PrOs <sub>4</sub> Sb <sub>12</sub>	Hybridization gap semiconductors ("Kondo insulators")
SmS, SmB <sub>6</sub> , CeOs <sub>4</sub> As <sub>12</sub> , UFe <sub>4</sub> Sb <sub>12</sub> , Ce <sub>3</sub> Bi <sub>4</sub> Pt <sub>3</sub>	Non-Fermi liquid behavior in f-electron materials
Y <sub>1-x</sub> U <sub>x</sub> Pd <sub>3</sub> , U <sub>1-x</sub> M <sub>x</sub> Pd <sub>2</sub> Al <sub>3</sub> (M = Y, La, Th), CeCu <sub>6-x</sub> Au <sub>x</sub> , YbRh <sub>2</sub> Si <sub>2</sub>	

R indicates a lanthanide element. This is a partial list that is based on the principal interests of our research group over these years.

## 2. Ferromagnetic superconductors

### 2.1. Interplay between superconductivity and localized moment ferromagnetism

An example in which several competing interactions produce an entirely new phenomenon is drawn from research carried out in the 1970s on the interplay between superconductivity (SC) and localized moment ferromagnetism (FM) in the ternary lanthanide intermetallic compounds ErRh<sub>4</sub>B<sub>4</sub> and HoMo<sub>6</sub>S<sub>8</sub> [1,2]. In these two compounds, the localized magnetic moments of the lanthanide ions (Er or Ho) on a sublattice that undergo FM order are coupled via a weak exchange interaction with the spins of electrons that reside within molecular units or "clusters" (Rh<sub>4</sub>B<sub>4</sub> or Mo<sub>6</sub>S<sub>8</sub>) that are responsible for the SC. Moreover, the SC and FM have comparable energies  $E_{SC} \approx k_B T_c$  and  $E_{FM} \approx k_B \Theta_C$ , where  $T_c$  is the SCing critical temperature and  $\Theta_C$  is the Curie temperature. It was found that the SC that occurs below a critical temperature  $T_{c1}$  vanishes (the compound reenters the normal state) at a lower critical temperature  $T_{c2}$  below  $\Theta_C$  (i.e.,  $T_{c2} < \Theta_C < T_{c1}$ ). The transition at  $T_{c2}$  exhibits thermal hysteresis and appears to be first order in character. The reentrant superconductive behavior of the compound ErRh<sub>4</sub>B<sub>4</sub> is illustrated in the electrical resistivity  $\rho(T)$  and magnetic susceptibility  $\chi_{ac}(T)$  data shown in Fig. 1, where  $T_{c1} = 8.7$  K,  $T_{c2} \approx 0.9$  K, and  $\Theta_C \approx 1.5$  K. Although SC is destroyed by FM at  $T_{c2}$ , neutron scattering experiments reveal that between  $T_{c2}$  and  $\Theta_C$ , SC coexists macroscopically in separate regions with FM and microscopically with a new sinusoidally modulated magnetic state with a wavelength of  $\lambda \sim 100$  Å. The sinusoidally modulated magnetic state is produced by the screening of the exchange and/



**Fig. 1.** The ac magnetic susceptibility  $\chi_{ac}$  and ac electrical resistance vs temperature for ErRh<sub>4</sub>B<sub>4</sub> in zero applied magnetic field. After Refs. [1,2].

or electromagnetic interactions at long wavelengths by the supercurrent. Neutron scattering measurements on a single crystal of ErRh<sub>4</sub>B<sub>4</sub> revealed that the sinusoidally modulated magnetic state in ErRh<sub>4</sub>B<sub>4</sub> is planar with the propagation vector oriented at an angle of 45° with respect to the *c*-axis and one of the *a*-axes with the Er magnetic moments aligned parallel to the other *a*-axis. Rich and complex phase diagrams are found upon substitution of other R ions at the Er site or other transition metal ions at the Rh site.

### 2.2. Interplay between superconductivity and itinerant ferromagnetism

Recently, several compounds have been found which exhibit the coexistence of SC and itinerant FM with  $T_c \ll \Theta_C$ , in contrast to ErRh<sub>4</sub>B<sub>4</sub> and HoMo<sub>6</sub>S<sub>8</sub>, which display reentrant SCing behavior with  $T_{c2} < \Theta_C < T_{c1}$ . This behavior was first observed in UGe<sub>2</sub> [3,4] under pressure and, subsequently, in URhGe [5–7] and UCoGe [8,9] at atmospheric pressure. For the  $T$ – $P$  phase diagram of UGe<sub>2</sub>, the SC resides within the FM phase between 9 kbar and the critical pressure  $P_c \approx 16$  kbar at which  $\Theta_C$  vanishes and appears to owe its existence to the occurrence of the FM. The line that intersects the SCing dome delineates another FM phase at lower  $T$  and  $P$  with a smaller ordered moment. Based on experiments performed on a single crystal with a mean free path  $l \gg \xi$ , it was concluded that spin-triplet p-wave SC and FM coexist in a microscopic manner in UGe<sub>2</sub>. On the other hand, from experiments made on polycrystalline samples with  $l \approx \xi$  which showed no decrease in  $T_c(P)$ , it was concluded that spin-singlet s-wave SC may coexist in an inhomogeneous fashion with the FM in UGe<sub>2</sub> [10]. Moreover, the SCing transitions are rather broad and only sharpen near 12 kbar where the specific heat jump at  $T_c$  is also a maximum, suggesting that the SCing fraction is largest there. The interplay between SC and FM in URhGe and UCoGe, which occurs at ambient pressure, appears to be rather different than it is in UGe<sub>2</sub>. Numerous issues remain to be addressed concerning the physics of the interplay of SC and itinerant FM in these and other compounds that remain to be discovered, yielding many opportunities for future research.

## 3. Interplay between superconductivity, charge, spin or exotic density waves and magnetism

Another example of the competition between different types of order is the interrelation of SC and charge density (CDW) or spin

density (SDW) waves. This is most often observed in low dimensional (2D or 1D) systems, which have a proclivity for CDW or SDW formation.

A particularly interesting example of the competition between SC and an ordered phase that has the earmarks of a density wave (DW), but has yet to be identified, is found in the heavy fermion superconductor URu<sub>2</sub>Si<sub>2</sub> [11,12]. This compound has a moderately high electronic specific heat coefficient  $\gamma \approx 112$  mJ/mol K<sup>2</sup> above a temperature  $T_0 = 17.5$  K, below which there is a pronounced second-order mean-field anomaly in  $C(T)$ , characterized by a “jump”  $\Delta C \sim 2.9\gamma T_0$  at  $T_0$  and an exponential region  $C(T) \sim \exp(-\Delta/T)$  with an energy gap  $\Delta \sim 100$  K below  $T_0$ . However, the entropy  $\Delta S \approx 0.2R \ln 2$  of this phase is too large for it to be identified with the AFM phase that also forms below  $T_0$ , which has a very small staggered moment  $\mu \approx 0.03\mu_B$ /U ion, according to neutron scattering experiments. Since the order parameter (OP) of this phase has not been identified, it is referred to as the “hidden order” (HO) phase. At lower temperature, SC occurs below  $T_c \sim 1.5$  K and coexists with the HO phase. Moreover, the value of  $\gamma$  is reduced to  $\sim 66$  mJ/mol K<sup>2</sup> for  $T < T_0$ , indicating that  $\sim 40\%$  of the Fermi surface is removed by the formation of the DW with the remainder of the Fermi surface removed by the SC at  $T_c$ . A great deal of effort is currently being expended by various groups to establish the phase diagram delineating the HO/small moment (SM) AFM, large moment (LM) AFM, SC, and paramagnetic (PM) phases and determine whether the small moment is intrinsic. There is evidence that the small magnetic moment in the SM AFM phase is actually associated with a small volume fraction  $V_f$  of a LM AFM phase where  $\mu \approx 0.4\mu_B$ /U ion and that  $V_f$  grows with pressure until it reaches unity at a critical pressure  $P_c$  that has been reported to range from about 6 to 15 kbar. Recent research in our laboratory suggests that there is a nearly vertical phase boundary at  $\sim 15$  kbar whose relationship with the HO/SM AFM–LM AFM transition is not yet clear. This partial gapping scenario seems to occur in many heavy fermion superconductors that exhibit some type of density wave (usually, a SDW) that coexists with SC at lower temperature.

#### 4. Quantum critical points, non-Fermi liquid behavior, and superconductivity

##### 4.1. Non-Fermi liquid behavior

Another example of materials driven physics is the discovery of non-Fermi liquid (NFL) behavior in the Y<sub>1-x</sub>U<sub>x</sub>Pd<sub>3</sub>, the first f-electron system in which NFL behavior was observed [13–16]. The NFL characteristics included an electrical resistivity  $\rho$  linear in  $T$ , a specific heat  $C$  divided by  $T$ ,  $C/T$ , that diverges as  $-\ln(T)$ , and a magnetic susceptibility  $\chi$  that varies as  $T^{1/2}$ . On the basis of the early studies of Y<sub>1-x</sub>U<sub>x</sub>Pd and other chemically substituted systems such as UCu<sub>5-x</sub>Pd<sub>x</sub>, CeCu<sub>6-x</sub>Au<sub>x</sub>, and U<sub>1-x</sub>Th<sub>x</sub>Pd<sub>2</sub>Al<sub>3</sub>, it was proposed that the NFL behavior of the low temperature physical properties is a general feature of certain f-electron materials. Several models have been proposed to account for the NFL behavior, including two single ion models, the quadrupolar Kondo and Kondo disorder models, and two interacting ion models, one involving fluctuations of an order parameter near a second order phase transition that has been suppressed to 0 K, and the Griffiths–McCoy model. Many properties of the Y<sub>1-x</sub>U<sub>x</sub>Pd<sub>3</sub> system are consistent with the quadrupolar Kondo effect, while others are indicative of quantum critical behavior associated with the spin glass (SG) QCP at  $x \approx 0.2$ . In addition to the chemically substituted systems, a number of stoichiometric (or nearly stoichiometric) compounds have been discovered which exhibit NFL behavior in their physical properties and are located

(in control parameter space) near a QCP (usually an AFM QCP). These include, for example, CeCu<sub>6-x</sub>Au<sub>x</sub>, YbRh<sub>2</sub>Si<sub>2</sub>, CeCoIn<sub>5</sub> and CeRhIn<sub>5</sub> (alloyed with Co or under pressure). It is interesting that the NFL characteristics observed for all of these systems are rather similar and include a power law  $T$ -dependence of  $\rho$  with an exponent  $n$  that is usually close to 1, a  $-\ln(T)$  divergence of  $C/T$ , a non-Curie–Weiss  $T$ -dependence of  $\chi$  that takes various forms such as a power law in  $T$  with an exponent of the order of 0.5, and an energy  $E$  divided by  $T$  scaling of the imaginary part of the dynamical susceptibility.

The nearly universal behavior of these properties in both chemically substituted and stoichiometric f-electron compounds suggests that there may be a more general theory to account for the NFL behavior in these systems. Also, in some systems, the NFL behavior persists to control parameter values that are far away from the QCP or does not even appear to be associated with a QCP. During the past several years, we have been exploring the types of behavior that occur near the FM quantum phase transition (QPT) in the system URu<sub>2-x</sub>Re<sub>x</sub>Si<sub>2</sub> [17,18]. As part of a systematic study of the effect of various transition metal substitutions on the HO phase and the SC in URu<sub>2</sub>Si<sub>2</sub>, we found that T<sub>c</sub> and Re substitutions produce a FM phase in which  $\Theta_c$ , the saturation moment  $m_s$  and  $\gamma$  exhibit a peak at  $x \approx 0.6$ . This behavior and the absence of features in  $\rho(T)$  and  $C(T)$  at  $\Theta_c$  suggest that the FM is itinerant in nature. In a study of the URu<sub>2-x</sub>Re<sub>x</sub>Si<sub>2</sub> system,  $\rho(T)$  and  $C(T)$  exhibit NFL characteristics that are more pronounced near the QCP associated with the onset of FM at  $x_c \approx 0.3$ , but also extend deep into the FM state to  $x \approx 0.6$ . The dynamical susceptibility, measured recently by means of inelastic neutron scattering, shows  $E/T$  scaling in the region of  $x$  where the NFL behavior in  $\rho(T)$  and  $C(T)/T$  is observed. Research is currently underway on characterizing the NFL behavior in single crystal specimens of URu<sub>2-x</sub>Re<sub>x</sub>Si<sub>2</sub>.

##### 4.2. Interplay of superconducting, density wave, and magnetic order in layered transition metal pnictides and other novel layered compounds

Recently, high  $T_c$  SC was reported in the system LnFeAs(O<sub>1-x</sub>F<sub>x</sub>) [19], where Ln is a lanthanide, with values of  $T_c$  as high as 55 K for Ln = Sm [20]. These materials are based on a class of compounds with a layered crystal structure of the form LnFePnO that were first synthesized by Jeitschko and coworkers with Pn = P [21] and As [22]. In these high  $T_c$  SCors, doping apparently suppresses the SDW in the parent LnFeAsO compound and gives rise to SC. Thus, in these materials, SC and the SDW apparently compete for the Fermi surface, similar to the situation in URu<sub>2</sub>Si<sub>2</sub>, discussed earlier. High  $T_c$  SC has also been observed in the related systems of the form (M<sub>1-x</sub>M<sub>x</sub>)Fe<sub>2</sub>As<sub>2</sub>, where M = alkaline earth, M' = alkali metal, with values as high as 38 K [23].

Superconductivity in LnFePnO compounds was discovered by Kamihara et al. [24] in LaFePO, and values of  $T_c$  ranging from 3 K [24] to 7 K [25] have been reported. However, in a recent study of polycrystalline materials, it was concluded that stoichiometric LaFePO is metallic but non-SCing [26] at temperatures as low as 0.35 K. We recently succeeded in synthesizing single crystals of LaFePO and found that they exhibited SC with  $T_c \approx 6.6$  K, according to electrical resistivity and magnetic susceptibility measurements [27]. However, we could not detect a specific heat jump at  $T_c$ , suggesting that only a small fraction of the sample is SCing or that the SCing transition of the bulk material is very broad. The SC appears to be a property of the single crystals, since the resistively measured upper critical field is quite anisotropic. Recently, measurements of the specific heat for single crystals of LaFePO revealed a jump at  $T_c$ , indicative of bulk SC [28].

High-pressure measurements performed in our laboratory [27] reveal that  $T_c$  passes through a maximum of nearly 14 K at  $\sim 110$  kbar, demonstrating that it may be possible to achieve significantly higher values of  $T_c$  in the phosphorus-based oxypnictides. Recently we discovered SC in LnFePO compounds with Ln = Pr and Nd [29]. Shown in Fig. 2 is a plot of  $T_c$  vs Ln in the LnFePnO systems for Pn = As and P.

We have also performed several high-pressure resistivity experiments on the SCors LaFeAs(O<sub>0.88</sub>F<sub>0.11</sub>) and CeFeAs(O<sub>0.88</sub>F<sub>0.12</sub>) [30]. At ambient pressure, these samples have onset  $T_c$ 's of 28 and 44 K, respectively. While the  $T_c$  of LaFeAs(O<sub>0.89</sub>F<sub>0.11</sub>) goes through a maximum between 10 and 68 kbar, in qualitative agreement with a recent report by Takahashi et al. [31], the  $T_c$  of CeFeAs(O<sub>0.88</sub>F<sub>0.12</sub>) decreases monotonically over the measured pressure range. At 265 kbar, the  $T_c$  of the cerium-based compound has been suppressed below 1.1 K. Based upon these and other measurements reported in the literature, it appears that  $T_c$  vs  $P$  in the transition metal pnictides has a “dome shape” similar to  $T_c$  vs charge carrier concentration in the high  $T_c$  cuprate SCors and  $T_c$  vs  $P$  in heavy fermion SCors in the vicinity of AFM QCPs.

In a related study, we have recently performed measurements of  $\rho(T)$  under pressure on the compound TbTe<sub>3</sub> [38]. The LnTe<sub>3</sub> compounds have a layered structure that consists of stacks of LnTe layers and Te planes. These materials have attracted a great deal of recent interest because they exhibit two CDW transitions [39], one at a higher temperature with a propagation vector along the  $c$ -axis, and the other at a lower temperature with a propagation vector that is orthogonal to the CDW that forms at higher temperature, so that at lower temperature the CDWs have a “rectangular” configuration. Our measurements of  $\rho(T, P)$  in TbTe<sub>3</sub> have revealed a phase diagram where the two CDW transitions converge at about 20 kbar, the Néel temperature  $T_N$  of the AFM phase that occurs at lower  $T$  has a weak  $P$ -dependence, and SC is found to occur above 20 kbar with a  $T_c$  that is weakly  $P$ -dependent. Near 20 kbar, the CDW, AFM, and SC transitions coexist, while above 20 kbar, only SC is observed. A particularly interesting aspect of this study is that these compounds apparently represent a new class of pressure-induced magnetically ordered SCors. The CDW and SCing phases in TbTe<sub>3</sub> appear to compete for the Fermi surface, similar to the situation observed in URu<sub>2</sub>Si<sub>2</sub>, in which the HO and SCing phases compete for the FS.

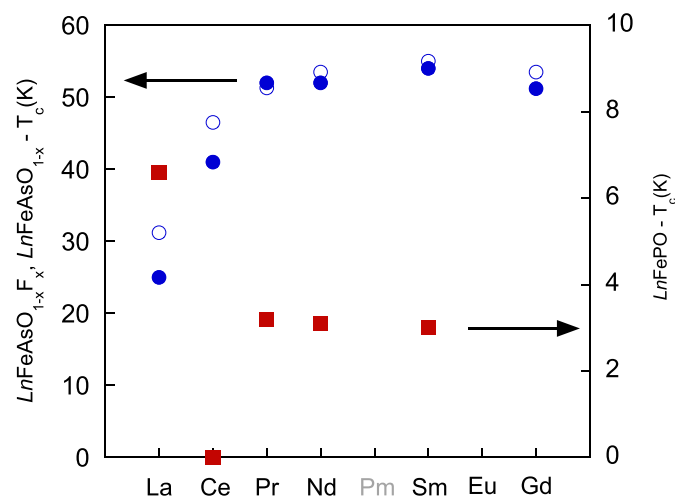


Fig. 2. A comparison of the evolution of the SCing transition temperature  $T_c$  vs lanthanide Ln for the series LnFePO with Ln = La, Ce [32], Pr, Nd, Sm [33] (solid squares), the optimally fluorine doped compounds LnFeAsO<sub>1-x</sub>F<sub>x</sub> with Ln = La [19], Ce [34], Pr [35], Nd [36], Sm [20], and Gd [37] (solid circles), and the oxygen deficient compounds LnFeAsO<sub>1- $\delta$</sub>  [37] (open circles). After Ref. [29].

### 4.3. Vortex physics in cuprate high- $T_c$ superconductors

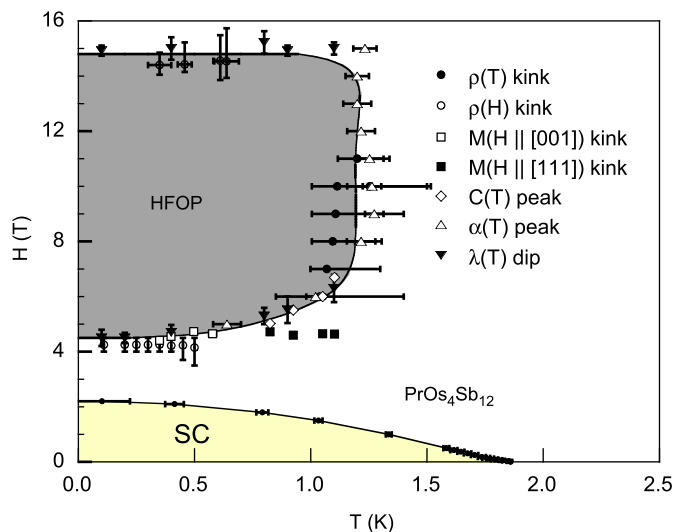
Another prime example of how new materials can further drive or even open up new areas of physics is the discovery in 1986 of high temperature SC by Bednorz and Müller in the Ba–La–Cu–O system [40]. Since 1986, nearly 20,000 journal papers addressing the phenomena of vortices in high-temperature SCors have been published. In the preceding 35 years, since the prediction of the existence of the magnetic vortex flux line in a certain type of superconductor by Abrikosov [41], less than 500 papers were published. Prior to 1986, vortices in SCors were more of a topic for theoretical consideration than of practical concern.

However, shortly after the discovery of Bednorz and Müller, investigation of the magnetic susceptibility revealed the existence of an region in the  $H$ – $T$  phase diagram where a reversible magnetic response in  $M(H)$  was observed between the diamagnetic onset of SC and a magnetically irreversible state [42]. This boundary between these two regions in the  $H$ – $T$  phase space is known as the irreversibility line  $H_{irr}(T)$ , wherein at fields/temperatures below  $H_{irr}(T)$  the vortex flux lines become immobile, “freezing” into a solid array. From the perspective of electrical transport properties, the zero resistance state is achieved by the formation of a solid ensemble of vortices. The boundary between the dissipationless SCing state and the resistively dissipative state, the “vortex liquid”, is known as a vortex-lattice or a vortex-glass melting transition, with the phase boundary denoted as  $H_m(T)$  or  $H_g(T)$ , respectively. Generally speaking there is agreement that the above phase boundaries  $H_{irr}(T)$  and  $H_m(T)$  or  $H_g(T)$  represent the same phenomenon. Since the location of  $H_g(T)$  in the phase diagram has consequences as to the utility of the material, i.e., its supercurrent carrying capacity, this boundary has been the subject of intense theoretical and experimental investigation for the past two decades.

Thousands of papers have attempted to address the nature of the solid vortex state and the transition to the liquid state including the seminal works of Blatter and Ivlev (BI) [43] and of Fisher, Fisher and Huse (FFH) [44]. A consistent theory describing the vortex-solid melting scenario over the entire vortex lattice melting line with a single expression has proven to be elusive for nearly twenty years. Recently however, we investigated the high magnetic field transport properties of Y<sub>1-x</sub>Pr<sub>x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6.97</sub> ( $x = 0.1, 0.2, 0.3, 0.4$ ) thin films in order to establish the magnetic field-temperature-Pr doping ( $H$ – $T$ – $x$ ) phase diagram [45,46]. These measurements led to the development of a new model, based upon the work of both BI and FFH, describing the conditions of the vortex solid–vortex liquid transition; i.e., an expression for the vortex-glass melting line  $H_g(T)$ . The expression for  $H_g(T)$  is able to conform to the entirety of the melting line data for these samples, as well as that of many other type-II SCors we examined. These results demonstrate that the mechanism of the melting of the vortex-solid can be described continuously over temperatures ranging from  $T_c$  down to the lowest temperatures examined ( $T \geq 0.03T_c$ ).

### 5. Strongly correlated electron behavior in filled skutterudites

The filled skutterudite compounds, which have the formula MT<sub>4</sub>X<sub>12</sub>, where M = alkali metal, alkaline earth, lanthanide, or actinide, T = Fe, Ru, or Os, and X = P, As, or Sb, have attracted a great deal of interest in recent years because they exhibit a wide range of correlated electron phenomena and are promising candidates for thermoelectric applications [47–49]. Correlated electron phenomena that have been observed include SC, magnetic order, quadrupolar order, valence fluctuations, heavy fermion behavior, non-Fermi liquid behavior, and hybridization



**Fig. 3.** The  $H$ - $T$  phase diagram for  $\text{PrOs}_4\text{Sb}_{12}$ . The SCing state (SC) phase boundary is derived from the electrical resistivity  $\rho(T, H)$  data. The high field ordered phase (HFOP) is deduced from features observed in  $\rho(T, H)$ ,  $C(T, H)$ ,  $M(T, H)$  ( $H \parallel [001]$  and  $[111]$ ), thermal expansion  $\alpha(T, H)$ , and magnetostriction  $\lambda(T, H)$ . After Refs. [51,50].

gap semiconductivity. We have focused on the lanthanide based filled skutterudites. The ground states of these compounds are apparently determined by a delicate interplay between hybridization of Ln localized 4f- and itinerant-electron states, crystalline electric field splitting of the Ln energy levels, magnetic and quadrupolar interactions, and electronic band structure. In particular, the compound  $\text{PrOs}_4\text{Sb}_{12}$  is of considerable interest for several reasons: (1) it exhibits SC with  $T_c = 1.85\text{K}$  that apparently develops out of a heavy Fermi liquid with a quasiparticle effective mass  $m^* \approx 50\text{me}$ , (2) it is the first example of a heavy fermion superconductor based on Pr (all of the other known heavy fermion SCors are compounds of Ce or U); (3) it displays some type of unconventional strong coupling SC that breaks time reversal symmetry, apparently consists of several distinct SCing phases, some of which appear to have point nodes in the energy gap, and may involve triplet spin pairing of electrons; (4) there is a high field ordered phase between 4.5 and 16T and below  $\sim 1\text{K}$  that has been identified with antiferroquadrupolar order, indicating that the SC occurs in the proximity of a quadrupolar quantum critical point, similar to the situation with certain Ce and U compounds where SC is found in the vicinity of an antiferromagnetic (AFM) QCP; and (5) the pairing of SCing electrons may be mediated by electric quadrupole fluctuations, rather than magnetic dipole fluctuations, which are believed to be responsible for pairing in the Ce and U based heavy fermion SCors [50,51]. (Fig. 3)

In contrast, the compound  $\text{PrOs}_4\text{As}_{12}$  undergoes transitions at 2.3 and 2.2K in zero-field into two ordered phases that can be suppressed to 0K with magnetic fields of 2 and 3.2T. The low field ordered phase is antiferromagnetic, while the nature of the higher field ordered phase has not yet been determined. The temperature and field dependences of the specific heat and electrical resistivity indicate that  $\text{PrOs}_4\text{As}_{12}$  is a Kondo lattice system with a small Kondo temperature  $T_K \sim 1\text{K}$  and an enormous electronic specific heat coefficient of  $\sim 1\text{J/molK}^2$  [48].

## 6. Concluding remarks

In this paper, we have described several examples of new phenomena, some of which involve the interplay between

competing interactions, that were driven by the development of new materials. We also identified several directions in which there are opportunities for further research. These include the (1) the occurrence of SC in itinerant ferromagnets, (2) the identification of the HO phase and the  $T$ - $P$  phase diagram of  $\text{URu}_2\text{Si}_2$ , (3) the competition between CDW or SDW and SCing phases for density of states on the FS, (4) the possibility of new SCing electron pairing mechanisms, such as electric quadrupole fluctuations, as suggested by the unconventional SC of the heavy fermion compound  $\text{PrOs}_4\text{Sb}_{12}$ , (5) the occurrence of NFL behavior deep in the FM state in the  $\text{URu}_{2-x}\text{Re}_x\text{Si}_2$  system, (6) the development of a general theory of NFL behavior that accounts for the typical NFL characteristics found in chemically substituted and stoichiometric f-electron materials. It seems clear that further developments in the materials area will lead to the discovery of new phenomena and the elucidation of known phenomena in the future.

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