Theory of "ferrisuperconductivity" in U_{1-x}Th_{x}Be_{13}

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We construct a two component Ginzburg-Landau theory with coherent pair motion and incoherent quasiparticles for the phase diagram of U_{1-x}Th_{x}Be_{13}. The two staggered superconducting states live at the Brillouin zone center and the zone boundary, and coexist for temperatures $T \leq T_{c2}$ at concentrations $x_{c1} \approx 0.02 \leq x \leq x_{c2} \approx 0.04$. We predict below $T_{c2}$ appearance of a charge density wave (CDW) and Be-sublattice distortion. The distortion explains the $\mu$SR relaxation anomaly, and Th-impurity mediated scattering of ultrasound to CDW fluctuations explains the attenuation peak.

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Introduction: Heavy fermion materials continue to receive intense experimental and theoretical interest \cite{1}. In particular, the rather spectacular properties of the heavy fermion superconductor alloy U_{1-x}Th_{x}Be_{13} have defied a comprehensive theoretical understanding for over 15 years. In this system, the temperature ($T$) vs. concentration ($x$) plane displays four distinct ordered phases, as shown schematically in Fig. 1 \cite{1-3}. Pressure studies \cite{4,5}, lower critical field data \cite{6}, and the size of the specific heat anomalies \cite{1} strongly suggest that all of these phases are associated with superconductivity. However, below $T_{c2}$, local magnetic probe experiments \cite{2} reveal an anomaly presumed to arise from weak magnetism with ordered moment $\mu \approx 0.01\mu_B$. Longitudinal ultrasound attenuation ($\alpha_s$) data display a peak, two orders of magnitude above the normal state background, which contrasts with an $\alpha_s$ drop in standard superconductors \cite{7}. The normal state of this system is also anomalous. The resistivity of UBe\textsubscript{13} is reproducibly large (order 100 $\mu\Omega$-cm) at $T_c$ and non-Fermi liquid (NFL) like in its temperature dependence \cite{1}(a). \cite{7}. Fermi liquid behavior and a small resistivity are restored by application of magnetic field and pressure, suggesting that this residual resistivity is intrinsic \cite{8}. These results legislate against an interpretation of the superconductivity of UBe\textsubscript{13} in terms of pairing within a traditional Fermi liquid quasiparticle background. Rather, there is electron pair coherence, but electron quasiparticle incoherence, similar to the interlayer tunneling and “stripe” theories of cuprate superconductivity.

In this paper, we propose a new phenomenological theory for superconductivity in U_{1-x}Th_{x}Be_{13} which explains many of the observed data and also is consistent with the NFL normal state. Motivated by results for the two-channel Kondo impurity \cite{9}(a), \cite{9} and lattice \cite{10,11} models, we develop a phenomenology in which localized and presumed odd-frequency pairing excitations hop coherently on the lattice, but with negative pair hopping/Josephson coupling from site to site. Our main result is that the low temperature phase below $T_{c2}$ is a ferrisuperconductor, with spatially modulated pair amplitude and coexisting superconducting order parameters with zone center and zone boundary center of mass momentum. The name derives from obvious analogies to ferrismagnetism. Moreover, the ferrisuperconductivity induces concomitant charge density wave (CDW) and volume conserving antiferrodistortive (AFD) order. The combined ordering allows us to quantitatively explain the anomalies observed in $\mu$SR relaxation \cite{2} and $\alpha_s$ \cite{7} experiments while invoking no magnetic moments in the low temperature phase. For $\alpha_s$, our phenomenology is constrained by experiment and microscopic theory, leaving one adjustable parameter to provide an excellent fit to both the temperature and frequency dependence. Our theory has several testable predictions.

Microscopic motivations: The two-channel Kondo (Anderson) lattice model, which has been rigorously solved using dynamical mean field theory in infinite spatial dimensions \cite{12}, \cite{13}, has been shown to display many properties consistent with UBe\textsubscript{13}. This model consists of local spin 1/2 moments coupled antiferromagnetically to two species of conduction electrons, derived here from the quadrupolar Kondo effect \cite{14}(a). This model naturally explains the NFL thermodynamics and transport properties of the normal phase. The calculations also confirm the possibility of an odd-frequency superconducting state \cite{15}, as anticipated from the strong local pairing fluctuations in the impurity model \cite{9}(a), \cite{9}. The relevant excitations of the normal state are not conventional Landau quasiparticles, so coherent single particle transport is irrelevant.

Ginzburg-Landau Theory: To characterize the various superconducting states we construct a Ginzburg-Landau functional. Assuming the superconductivity is induced by two-channel Kondo effect induced pairing interactions at the U sites \cite{9}, one can argue that the resulting order parameters should be odd in frequency, and staggered in real space \cite{16}. To identify candidate order parameters we investigated a negative pair hopping model with third nearest neighbor overlap, and assumed a logarithmically divergent local pairing susceptibility at the U sites \cite{17}. The local symmetry of these pairing or-
FIG. 1. Sketch of the different superconducting regions and the corresponding theoretical order parameters for U_{1-x}Th_xBe_{13}. Here, x_{c1} \approx 0.02 and x_{c2} \approx 0.04. The maximum of T_{c1} is T_{c1,\text{max}} \approx 0.6 K. \alpha_x peak{s at T_{c2}}, and the muon relaxation rate decreases below T_{c2}. In our theory, for T < T_{c2} a CDW and a lattice distortion are generated, which account for these data.

order parameters about the U-sites is A_2 \[15\]. Given the two-sublattice fcc structure of UBe_{13}, two possible order parameters emerge [4]: \eta_Γ which sits at the Brillouin zone center, and the three dimensional order parameter \eta_\Gamma which lives at the three X points \Gamma_i at the center of the square faces of the fcc Brillouin zone. These order parameters transform as the odd parity \Gamma - and even parity \Gamma point reps of the \Gamma_0 (Fm\bar{3}c) space group of UBe_{13}. As shown in Fig. 2, \eta_\Gamma changes in sign from site to site on the simple cubic U-sublattice, while \eta_\Gamma has lines of alternating phase parallel to \Gamma_i.

The resulting free energy functional invariant under time reversal, gauge and space group operations reads:

\[
\begin{align*}
F_0 &= \alpha^X \sum_{i=1}^{3} |\eta_i|^2 + \alpha^X \sum_{i=1}^{3} |\eta_i|^4 + \beta^X \sum_{i=1}^{3} |\eta_i|^4 \\
&+ \beta^\Gamma \sum_{i \neq j}^{3} |\eta_i|^2 |\eta_j|^2 + \beta^\Gamma \sum_{i \neq j}^{3} |\eta_i|^2 |\eta_j|^2 + F_{\Gamma \times X}, \quad (1) \\
F_{\Gamma \times X} &= \xi \sum_{i=1}^{3} |\eta_i|^2 |\eta_i|^2 + \zeta \sum_{i=1}^{3} (\eta_i^2 \eta_i^2 + c.c.) \quad (2)
\end{align*}
\]

As usual, we assume linear temperature dependence in the quadratic coefficients, viz., \alpha^X = a_1(T - T_{cX}) and \alpha^\Gamma = a_2(T - T_{c\Gamma}).

Our conjectured phase diagram is shown in Fig. 1. For pure UBe_{13}, analysis of observed anisotropies in the upper critical field data [16] lead us to identify the \eta_i-phases as likely candidates [17]. Pressure experiments strongly suggest that for x_{c1} \leq x \leq x_{c2} the lower temperature phase represents a continuation of the low concentration line [18]. Next, we conjecture that Th doping produces a relative stabilization of the \eta_i phase at intermediate concentrations, so that \eta_i and \eta_\Gamma coexist for x_{c1} \leq x \leq x_{c2} and T \leq T_{c2}. Given \eta_x and \Gamma point order parameter coexistence, we call this state ferrisuperconductivity in analogy with ferrimagnetism.

The parameters, \beta^X, \xi and \zeta in Eqs. (1) and (2) are not known a priori, but they are largely constrained by the physical properties of U_{1-x}Th_xBe_{13}. Since there is no CDW formation, time reversal symmetry breaking, or splitting of the transition under applied stress in pure UBe_{13} [5], the \beta^X's must satisfy \beta^X_2 > \beta^X_3 and \beta^\Gamma_2 < \beta^\Gamma_3 - \beta^\Gamma_1, yielding a phase with a single \eta_0 condensed.

The nature of the coexistence phase depends on the sign of \zeta. For \zeta > 0 we find a time reversal broken coexistence phase, where microscopic current loops induce interstitial antiferromagnetic order, a possibility noted previously for UPt_3 [6]. This could explain the observed \mu SR anomaly. However, it is more difficult to explain the observed large peak in \alpha_x at T_{c2} [7]. For \zeta < 0 the mixed superconducting state is completely different: in this case a CDW and a staggered lattice distortion appear below T_{c2} and the cubic symmetry of the lattice is lowered to tetragonal (see Fig. 1). The CDW arises because the phasing of the \eta_x, \eta_\Gamma order parameters corrugate the pair amplitude locally, producing a \pm |\eta_x| |\eta_\Gamma| alternation from plane to plane perpendicular to \Gamma_i (see Fig. 2).

The anomalies of the second transition can be explained consistently and easily for \zeta < 0: the lattice distortion can produce the observed increase in the \mu SR relaxation, while the peak in \alpha_x results from coupling to large induced CDW fluctuations.

Henceforth, we concentrate on the coexistence phase of U_{1-x}Th_xBe_{13}. To estimate the amplitude of the CDW (\gamma_i) and the displacement of the face Be atoms (u_i) we first construct the corresponding symmetry allowed coupling term in the Ginzburg-Landau functional:

\[
F_{\gamma - \eta - u} = \gamma_0^{-1} \sum_{i=1}^{3} \frac{\gamma_i^2}{2} + K_u \sum_{i=1}^{3} \frac{u_i^2}{2} + \gamma \sum_{i=1}^{3} \gamma_i u_i + \lambda \sum_{i=1}^{3} \gamma_i (\eta_\Gamma \eta_i^* + c.c.), \quad (3)
\]

where the u_i's and the \gamma_i's form three dimensional X_i = \Gamma_2 \otimes X_3 \times X point reps. The coupling \gamma \approx 0.4 eV/\AA and the spring constant \lambda \approx 2 \times 10^3 K/\AA^2 can be obtained from microscopic Thomas-Fermi theory calculations and from the bulk modulus, respectively, while \lambda \approx 10 K is estimated from the relative shift of T_{c2} and \chi_\mu^{-1} \approx 900 K is extracted from fits to the experimental data.

As we discuss below, from the \mu SR experiments we estimate a T = 0 K lattice displacement amplitude \gamma_0 = 0.4 \AA for Be on planes perpendicular to \Gamma_i. Using Eq. (3) a simple calculation yields an associated CDW amplitude of \gamma_i \leq 1.5, where we simplistically use \gamma_0 in the spring energy to produce an upper bound. This CDW amplitude is quite large at first sight. However, the charge is distributed among the 24 face Be sites surrounding the
U ion, resulting in an excess charge of $\sim 0.1 e/Be$. $u_0$ is somewhat large, but in view of the large lattice constant $a \approx 10\,\text{Å}$, is in reasonable agreement with observed displacements in CDW systems \cite{14}. Moreover, it is staggered and volume conserving (to first order).

The displacement does result in an increased $\mu$SR dephasing rate below $T_{c2}$, with reasoning as follows: The muon sits in the center of the Be(II) plaquettes \cite{20}. Be plaquettes on faces parallel to $\vec{Q}_1$ are alternately compressed and expanded. The dominant spin-dephasing mechanism of the muons is due to the dipolar coupling to Be nuclei, and varies in quadrature as $R^{-6}$, where $R$ is the muon-nearest-Be separation. Thus, muons in expanded/compressed plaquettes will experience reduced/enhanced relaxation. Averaging over inequivalent stopping sites, leaves only even powers of $u_0$, and coupling to compressed plaquettes dominates leading to an increase in dephasing. The resulting change in the muon relaxation rate $\sigma_{K T}$ is given, to leading order in $u_0$, by

$$\frac{\delta \sigma_{K T}}{\sigma_{K T}} \approx B u_0^2 = B \frac{4\lambda^2 \gamma^2}{(\chi_0^{-1} K - \gamma^2)^2} |\eta|^2 |\eta_0|^2,$$  

with $B \approx 0.4\,\text{Å}^{-2}$. Taking $u_0 = 0.5\,\text{Å}$ yields the estimated zero temperature relaxation rate increase of $\sim 10\%$; extending Eq. (4) to all orders in $u_0$ gives $u_0 \approx 0.4\,\text{Å} = 0.04a$, in rough agreement with NMR imposed constraints \cite{21}. The leading order scaling with $\eta_0^2$ is in excellent agreement with the experimental observations \cite{3}.

Now we analyze the anomalous peak in $\alpha_s$. As shown in Ref. \cite{3}, $\alpha_s$ is practically the same for (100) and (111) propagation directions, ruling out the domain wall dissipation mechanism of Refs. \cite{22,23}. The original experimental reference \cite{3} (and recent interpretation of thermal expansion data \cite{13}) suggest that the transition below $T_{c2}$ is purely magnetic, citing large moment Gd and Mn based metallic and insulating magnets with $\alpha_{s, mag} \approx 10\,\text{dB/μsec}$ at these frequencies. However, for magnetic coupling, the two primary contributions to attenuation are from energy relaxation (which varies like $\mu^2$), and order parameter fluctuations (which varies as $\mu^4$) \cite{23}. These mechanisms are incorrect in temperature dependence and magnitude: given $\mu \lesssim 0.01\mu_B$ from $\mu$SR \cite{2}, we find $\alpha_s \lesssim (0.1\mu_B/5\mu_B)^2 \alpha_{s, mag} = 4 \times 10^{-5}\,\text{dB/μsec}$, four orders of magnitude too small.

In view of these results, and the above interpretation of the $\mu$SR anomaly, we propose that the $\alpha_s$ peak is due to the strong interaction of the impressed phonons with CDW fluctuations at the Th sites. Sound waves propagate with a momentum $\vec{q} \approx 0$, and therefore can linearly couple to the CDW fluctuations at the $X$ points of the Brillouin zone only via the Th impurities at sites $\{ \overline{R}_{imp} \}$. The strongest coupling mechanism we find results from the destruction of the superconductivity and thus the CDW at the non-magnetic Th sites, with coupling.
\[ \Delta H = g \sum \sum_{\vec{R}_{\text{imp}}} \frac{3}{2} \vec{\omega} \cdot \vec{u}(\vec{R}_{\text{imp}}) \phi_{\omega}(\vec{R}_{\text{imp}}), \]

where \( \vec{u} \) denotes the acoustic displacement field and \( g \approx 0.8 \) eV is estimated from microscopic model calculations. \( \alpha_s \) is obtained from the imaginary part of the acoustic phonon self energy, shown to leading order in Fig. 3. Replacing the CDW bubbles by the renormalized static susceptibility, \( \chi_\omega = \chi_0/(1 - \gamma^2 \chi_0/K) \), and assuming a quadratic dispersion of the form \( \omega(k) = C|T - T_{c2}| + D s k^2 + D \pi k^2 \) with a cutoff energy \( E_c \sim 1K \) we can integrate out the internal momenta and we arrive at the following expression:

\[ \alpha_s \approx \text{Im}\{\Pi(\omega)\} = C x^2 \frac{\lambda^2|\eta|^2}{M c^2} \frac{\Delta^2}{\omega^2} I(\omega; T), \]

\[ I = \frac{3}{2} \int_0^1 dx \frac{\sqrt{x}}{\left(\frac{\alpha_s}{c} + c x^2\right)^2 + 4 \Delta^2 \omega^2}, \]

with \( C \) a number of the order of unity. To derive Eq. (6) we assumed a hydrodynamic damping \( 1/\tau \approx \omega \Gamma \) for the superconducting fluctuations. \( \Gamma \) is the only undetermined parameter in Eq. (6); all others are fixed by microscopic model estimates or experimental constraints [25]. Substituting the different couplings into Eq. (6) we estimate the prefactor to be \( 20 \frac{\Gamma}{\Delta} \) dB/\( \mu \)s, which is in very good agreement with the experiments (away from criticality, the overall magnitude is considerably reduced by the integral in Eq. (6)). Note that: (i) \( \alpha_s \) is asymmetric about the transition due to the \( \eta^2 \) factor; (ii) for \( \omega \to 0 \), \( \alpha_s \sim \frac{|T - T_{c2}|}{T_{c2}} \) away from \( T_{c2} \); (iii) for \( T = T_{c2} \) \( \omega \to 0 \), \( \alpha_s \sim \omega^{3/2} \). We obtain a fit of remarkable quality to the \( \alpha_s \) data of Ref. [23], as shown in Fig. 3.

**Predictions and further considerations:** Our theory admits a number of falsifiable predictions below \( T_{c2} \): (1) The Be displacements with magnitude \( \leq 0.4 \AA \) should be easily observable in neutron scattering experiments. (2) The impurity scattering mechanism produces an isotropic angular dependence for \( \alpha_s \) above \( T_{c2} \) and zero attenuation for transverse ultrasound, consistent with the rough agreement between longitudinal attenuation coefficients along the (100) and (111) directions measured for different samples of comparable nominal composition [23]. We anticipate an order of magnitude difference between longitudinal and transverse attenuation. (3) The \( \alpha_s \) peak will be maximized at the concentration \( x \approx 0.03 \) and drop significantly in magnitude near \( x_{c1}, x_{c2} \). Assuming insignificant variation of electronic parameters as a function of \( x \), then \( \alpha_s(x)/(T_{c1}(x) - T_{c2}(x)) \) should vary as \( x \) according to Eq. (6). This may provide a test of the impurity scattering mechanism. (4) The observed NMR line broadening below \( T_{c2} \) of Ref. [22] was originally attributed to the flux lattice, but this is ruled out by subsequent penetration depth data [23]. The broadening is roughly consistent with field gradient shifts due to our proposed Be sublattice distortion.

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[1] a) D.L. Cox and A. Zawadowski, Adv. Phys. 47, 599 (1998); (b) J. A. Sauls, Adv. Phys. 43, 113 (1994); (c) N. Grewe and F. Steglich, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneider, Jr. and L. Eyring (Elsevier, Amsterdam, 1991), Vol. 14.
[2] R.H. Heffner et al., Phys. Rev. Lett. 65, 2816 (1990).
[3] F. Kromer et al., Phys. Rev. Lett. 81, 4476 (1998).
[4] S. E. Lambert et al., Phys. Rev. Lett. 57 1619 (1986).
[5] R. Zieve et al., Phys. Rev. Lett. 72, 756 (1994).
[6] B. Batlogg et al., Phys. Rev. Lett. 55, 1319 (1985); D. Bishop et al., Phys. Rev. Lett. 57 2995 (1986).
[7] M. Aronson et al., Phys. Rev. Lett. 63, 2311 (1989); B. Batlogg et al., J. Mag. Mag. Mat. 63&64, 441 (1987).
[8] S. Chakravarty and P.W. Anderson, Phys. Rev. Lett. 72, 3859 (1994); S.A. Kivelson et al., Nature 393, 550 (1998); A.H. Castro-Neto and F.J. Guinea, Phys. Rev. Lett. 80, 4040 (1998).
[9] V.J. Emery and S. Kivelson, Phys. Rev. B 46, 10812 (1992).
[10] F. Anders et al., Phys. Rev. Lett. 78, 2000 (1997); M. Jarrell et al., Phys. Rev. Lett. 77, 1612 (1996).
[11] M. Jarrell et al., Phys. Rev. Lett. 78, 1996 (1997).
[12] P. Coleman et al., Phys. Rev. B 49, 8955 (1994).
[13] R. Heid et al., Phys. Rev. Lett. 74, 2571 (1995); V. Martisovits, and D.L. Cox, Phys. Rev. B 57, 7466 (1998).
[14] With third nearest neighbor hopping included, the leading order gradient free energies of both order parameters can be made locally stable.
[15] D.L. Cox and A.W.W. Ludwig, unpublished; see also Sec. 9.4.3 of Ref. [23](a).
[16] F. G. Aliev et al., J. Low Temp. Phys. 85, 359 (1991).
[17] V. Martisovits et al., to be published.
[18] R. Heid et al., Physica B223&224, 33 (1996).
[19] G. Gruner, *Density Waves in Solids* (Frontiers in Physics, Addison-Wesley, 1994).
[20] R.H. Heffner, private communication (1999).
[21] D.E. MacLaughlin et al., Phys. Rev. Lett. 53, 1833 (1984).
[22] R. Joynt et al, Phys. Rev. Lett. 56, 1412 (1986).
[23] The Landau-Khalatnikov mechanism ( K. Miyake and C.M. Varma, Phys. Rev. Lett. 57, 1627 (1986)) fails to an absent peak at \( T_{c1} \).
[24] K. Kawasaki in *Phase Transitions and Critical Phenomena*, vol. 5A, eds. C. Domb and M.S. Green (Academic Press, New York, 1976).
[25] We assume full reduction of the CDW amplitude at Th sites, which produces an upper bound to \( \alpha_s \).
[26] F. Gross-Alltag, Z. Phys. B82, 243 (1991).