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SUPERCONDUCTING PROPERTIES OF ACTINIDE COMPOUNDS AND OTHER RECENT RESULTS

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Resistivity of (Th, U)Be_{13} under pressure may show the restoration of the onset of electron coherence. Unseparated rare earth elements can be used for preparation of high-T_c superconductors.

The actinide elements lie between the 4f-electron and 3d-electron series in terms of the localization of their electrons. That is, the 5f series begins with transition metal behavior, and the 5f electrons form energy bands because of wavefunction overlap. This leads to superconductivity as in transition metals. Later in the series, as the 5f wavefunctions contract, local moments form as in most of the 4f-electron elements. In between these limits, there is a crossover of the behaviour, and there is uncertainty in the ground states of the materials. In compounds and alloys this uncertainty can be manipulated leading to much interesting physics [1].

In some uranium compounds where the uranium atoms are spaced far enough apart to prevent wavefunction overlap and where local moments are seen at high temperatures, an unusual superconducting ground state occurs [2]. This is heavy-fermion superconductivity, which was first observed in a cerium compound, $CeCu_2Si_2$ [3]. The large heat capacity observed at low temperatures, which would normally be associated with an ordering of the local moments seen at higher temperature, must be associated with the conduction band because the superconducting specific heat jump is proportional to the specific heat of the material before it becomes superconducting. How the local moment entropy is turned into conduction electron entropy in heavy-fermion compounds remains an important problem [2].

Local moments depress superconducting transition temperatures T_c's at a rate proportional to their total spin and not to their magnetic moments [4]. Two systems are known, UBe_{13} [5] and $REBa_2Cu_3O_x$ [6], in which neither the total spin nor the magnetic moments have any measurable effects on T_c's. In the heavy-fermion compound UBe_{13} however, small amounts of completely non-magnetic thorium produce a non-monotonic T_c depression and a complex array of behavior that is still not fully explored [7]. The thorium expands the lattice. It seemed possible that hydrostatic pressure could shift the resistive behavior of thorium-doped material back towards that of pure UBe_{13}. Fig. 1 shows the resistance of a 3.4 at% Th sample up to a pressure of 14.9 kbar, which is more than adequate to restore the lattice parameter. The return of the low temperature increase, and the

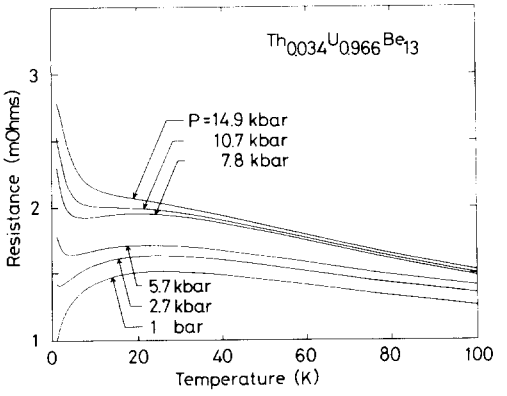

Fig. 1. The resistance of $Th_{0.034}U_{0.966}Be_{13}$ from 1.6 to 100 K at various hydrostatic pressures.

presumed onset of coherence, suggests a trend back to pure UBe_{13}. Unfortunately, preliminary measurements on a 3.4 at% Lu sample, which has a smaller lattice than UBe_{13}, show the same increase. Further measurements are underway to attempt to understand the effects of pressure on the resistivity of doped UBe_{13}.

As mentioned earlier, the high-T_c compounds made with various rare earths (RE) show no effects on T_c from the presence of local moments. Kishio et al. demonstrated that mixtures of rare earths also make high-T_c superconductors, and hence, that a significant cost-saving is possible because the rare earth elements need not be separated [8]. We have confirmed this measurement with a different mixture of unseparated rare earths with the trivial difference of beginning with a sesquioxide rather than carbonates. Our oxide contained (RE's only) 63 at% Y; 10 at% Yb; 7 at% each of Dy and Er; 4 at% each of Tm and Gd; 1–2 at% each of Ce, Sm, and Ho; and approximately 0.5 at% each of La, Pr, Nd, and Lu. Samples prepared from submicron (sub-μm) powders that were both calcined and fired in O_2 at 950°C all showed T_c's above 90 K.

There have been very few detailed descriptions for preparing polycrystalline, bulk samples of $REBa_2Cu_3O_x$ in the works we have seen. It seems of value to mention some of the details that we have found to be important for the mid-RE elements (Eu, Gd, Dy, Ho, Er). Starting materials are dried for many hours, CuO at 600°C and RE_2O_3 and $BaCO_3$ at 900–1000°C. Weights to a few percent are acceptable. If organic solvents that can contain water are used for cleaning, the items should be air dried carefully. The starting powders and calcined material are mixed for 12–72 hours in an agate ball mill that shakes the material vigorously. The calcined powder requires well over 24 hours to become predominantly sub-μm. This ball milling is extremely important for achieving single phase material. Mixed starting powder is packed loosely and calcined in air or O_2 for 12 hours or more at 980°C. Calcined, powdered material is then pressed and fired to 980°C in flowing O_2, cooled to 400°C (for convenience), and removed from the furnace. Times on the order of a few hours work for the treatment. Except for Gd, powders pressed at 2–3 kbar result in a final density of about 75%. For some reason Gd usually ends up at about 90%. Although we cannot explain this, it is quite useful.

Clearly the mid-RE's can be taken to higher temperatures than $YBa_2Cu_3O_x$, that is 30–60°C higher. We believe that this yields slightly better samples. As it seems that this cannot affect the oxygen stoichiometry, we suspect, that the extra temperature may help order the RE and Ba, which is clearly important to a high-quality sample. In attempting to quench samples of submicron calcined powder in air after brief heat treatments at 980°C in order to have lower-quality samples, we found that we could not get a T_c below 91 K. Thus, just as it is difficult to oxygenate high-density samples in weeks, it is trivial to oxygenate a submicron particle in seconds.

Finally, is their any relationship between heavy-fermion and high-T_c superconductivity? The discussions of what is the valence of copper and what is its moment certainly resemble the old arguments about cerium and uranium. Although the parameters do not seem much enhanced (except T_c) in the new materials [9], the small number of carriers do make them enhanced. Clearly strong electron–electron correlations are important in both classes of superconductors [10].

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References

[1] J.L. Smith, Z. Fisk and S.S. Hecker, Physica 130B (1985) 151.

[2] Z. Fisk, H.R. Ott, T.M. Rice and J.L. Smith, Nature 320 (1986) 124. Z. Fisk, D.W. Hess, C.J. Pethick, D. Pines, J.L. Smith, J.D. Thompson and J.O. Willis, to appear in Science.
[3] F. Steglich, J. Aarts, C.D. Bredl, W. Lieke, D. Meschede, W. Franz and H. Schäfer, Phys. Rev. Lett. 43 (1979) 1892.
[4] B.T. Matthias, J. Phys. Soc. (Japan) 17, suppl. B-1 (1962) 104.
[5] J.L. Smith, Z. Fisk, J.O. Willis, H.R. Ott, S.E. Lambert, Y. Dalichaouch and M.B. Maple, J. Magn. Magn. Mat. 63–64 (1987) 464.
[6] Z. Fisk, J.D. Thompson, E. Zirngiebl, J.L. Smith and S-W. Cheong, Solid State Commun. 62 (1987) 743.
[7] J.L. Smith, Z. Fisk, J.O. Willis, A.L. Giorgi, R.B. Roof, H.R. Ott, H. Rudigier and E. Felder, Physica 135B (1985) 3. J.L. Smith, Z. Fisk, J.O. Willis and H.R. Ott, to appear in Proc. 5th Conf. on Valence Fluctuations, Bangalore, India, January 1987 (Plenum, New York).
[8] K. Kishio, O. Nakamura, K. Kuwahara, K. Kitazawa and K. Fueki, Jap. J. Appl. Phys. 26 (1987) L694.
[9] M.K. Wu, J.R. Ashburn, C.T. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang and C.W. Chu, Phys. Rev. Lett. 58 (1987) 908.
[10] S-W. Cheong, S.E. Brown, Z. Fisk, R.S. Kwok, J.D. Thompson, E. Zirngiebl, D.E. Peterson, G.L. Wells, R.B. Schwarz, G. Gruner and J.R. Cooper, Phys. Rev. B 36 (1987) 3913. C.J. Pethick and D. Pines, to appear in Proc. Workshop on Superconductivity (Berkeley, CA, June 1987).