ELSEVIER

Synthetic Metals 103 (1999) 1795–1796

SYNTHETIC METALS

The Anomalous Superconducting Phase Diagram of $(BEDO\text{-}TTF)_2ReO_4 \cdot H_2O$.

C. C. Agosta[a], S. Ivanov[a], Z. Bayindir[a], T. Coffey[a], N. D. Kushch[b], E. B. Yagubskii[b], T. Burgin[c], and L. K. Montgomery[c]
[a]*Department of Physics, Clark University ,Worcester , MA, 01610, USA, http://physics.clarku.edu*
[b]*Institute of Chemical Physics, Chernogolovka, Russia*
[c]*Indiana University , Bloomington, Indiana, USA*

Abstract

We have measured the critical magnetic fields in the quasi 2D superconductor $(BEDO\text{-}TTF)ReO_4{\cdot}H_2O$ as a function of temperature with the magnetic field perpendicular and parallel to the conducting planes. A sharp positive change in the curvature, or kink, in the H-T phase line, similar to one in the phase diagram of the superconductor $\lambda\text{-}(BETS)_2GaCl_4$ occurs in the low temperature part of the phase diagram near $T/T_C = 0.4$. These kinks in the H-T phase line could be the signature of a change in the superconducting order parameter. We discuss other possibilities, such as magnetic transitions, and why they are less likely to exist in these salts. To support our claims we also present recent data showing part of the H-T phase diagram of $\lambda\text{-}(BETS)_2GaCl_4$ with the applied magnetic field parallel to the conducting planes.

Keywords: Transport measurements, Superconducting phase transitions, Organic superconductor

1. Introduction

The microscopic mechanism for superconductivity, including the symmetry of the order parameter, is still an open question in organic conductors. Indeed, it is not clear if all organic superconductors have the same microscopic mechanism or symmetry of their order parameters [1][2]. One indication of the similarity or difference between different superconductors is the shape of the H-T phase diagram. We have measured the H-T phase diagram of the superconductor $(BEDO\text{-}TTF)ReO_4{\cdot}H_2O$ (BEDO) using resistivity and rf penetration depth. The phase line in BEDO has an abrupt upward change in slope, similar to the H-T phase diagram previously reported in $\lambda\text{-}(BETS)_2GaCl_4$ (BETS) [3]. These are the only two organic conductors that have shown this behavior, and this unique phase diagram suggests that similar physical phenomena exist in these two otherwise very different organic salts.

2. Experimental

A single sample was used to make simultaneous measurements of rf penetration depth and resistance in platelets of BEDO. The resistance was measured using a standard four terminal ac method. The contacts were made by fixing 15 micron gold wires to the sample with gold paint. The sample was placed inside a small coil that was connected in parallel to a capacitor and made to self resonate at 25 MHz with a tunnel diode. The magnetic field of the small coil was perpendicular to the conducting planes of the BEDO. We could relate the rf penetration to the frequency of the self resonant circuit using a simple formula [3], and find the superconducting transition using a method similar to the standard methods used to find the superconducting transition with resistance measurements. Fig. 1 shows a characteristic resistance and penetration depth curve at base temperature. The H_{C2} derived from either measurement yields the same value.

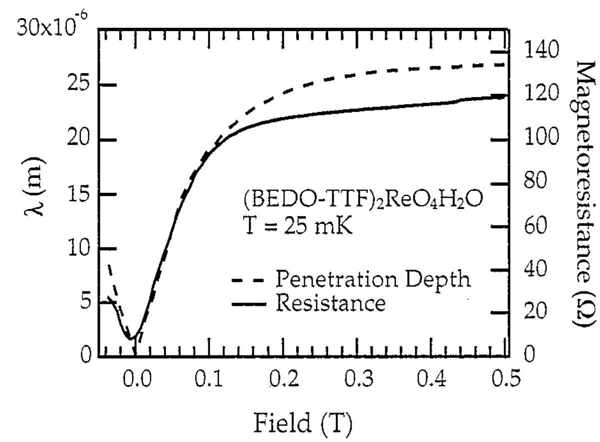

Fig. 1. The superconducting transition measured by both resistance and penetration depth.

3. Data

The phase diagram that results from these measurements is shown in Fig. 2. The upturn in the phase line occurs at ~T/Tc = 0.4. Four possible explanations exist for this type of phase diagram.

The first is dimensional crossover. To see the effects of dimensional crossover the sample would have to be oriented with the conducting planes parallel to the applied field [4]. It was easy to confirm that our measurements were made with the applied field perpendicular to the conducting planes, because the BEDO samples are platelets. The orientation was further verified by rotating the sample 90° and measuring a higher H_{C2} (= 0.8 T @ T = 25 mK) with the field parallel to the conducting planes.

The second explanation we considered was strong coupling. The existence of strong coupling is not very likely because the kink is too abrupt as compared to calculations that show a smooth transition to positive curvature [5], and also because the large electron phonon coupling would

PII: S0379-6779(98)00388-9

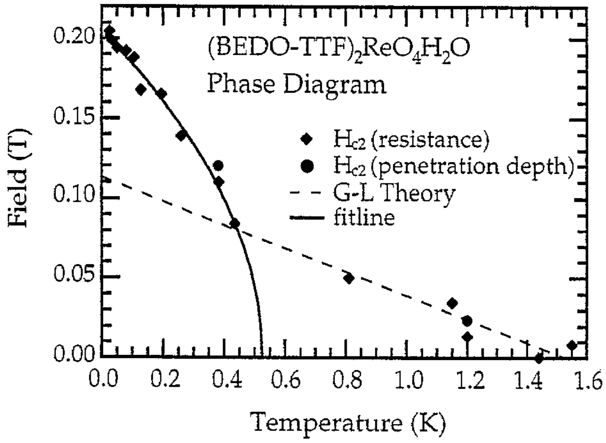

Fig. 2. The BEDO phase diagram.

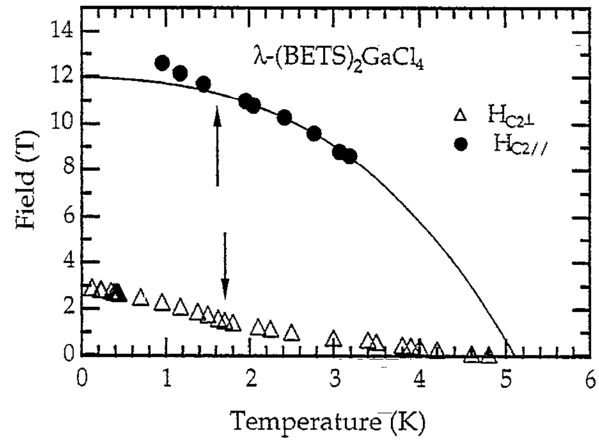

Fig. 3. The critical magnetic field in BETS with the magnetic field applied parallel to the conducting planes. The line is a guide to the eye and is extrapolated from the data. The ⊥ data from ref. [3] has a kink that is as obvious as the BEDO data, if seen on a more expanded scale.

enhance the effective mass, which we have measured to be near 1 for this salt [6].

Third we consider a magnetic transition, such as a dia or paramagnetic transition. A similar H-T phase diagram to BEDO was seen in the magnetic system $SmRh_4B_4$ [7]. Although the phase diagrams are very similar, there is no obvious magnetic ion in the BETS compound, and therefore a magnetic transition is not expected.

Rotating the sample with respect to the applied dc magnetic field and measuring the H-T phase diagram when the applied field is parallel to the conducting planes gives more information about a magnetic transition. If, for instance, the kink came from an anisotropic magnetic transition, the critical field for this transition would change as a function of angle. The internal fields, or spin orbit coupling, determine the force necessary to cant the spins and hence, the magnetic anisotropy of the salt. If, however, the kink came from a temperature induced transition, such as a superconducting order parameter shift, then the phase diagram with the applied field parallel to the conducting planes should have a kink at the same temperature as in the original perpendicular phase diagram.

We have preliminary H_{C2} data for the BETS salt with the applied magnetic field parallel to the conducting planes. The H-T phase diagram shown in Fig. 3 shows there is a positive slope change or kink in the parallel data at the same temperature as in previously measured perpendicular data [3]. This new data suggests that the kink is not dependent on magnetic field direction and is temperature induced. The transition still could be magnetic in origin if the magnetic moments are free to rotate in the crystal.

The fourth phenomena we have considered as an explanation of the kink in the phase diagram is a change in the superconducting order parameter. A similar phase diagram was seen in the UPt_3 heavy Fermion superconductor [8]. It was determined that the symmetry of the order parameter changed in UPt_3 as a function of temperature. The evidence for this type of transition in BEDO is not yet convincing, however thermal conductivity data for the BETS salt [3] has been reported that does support the hypothesis of two superconducting phases. Qualitatively the change in slope of the H-T phase line is consistent with a change in the order parameter. Consider a case where the symmetry of the order parameter changed from s-wave to d-wave. The s-wave portion for a BCS superconductor starts as a straight line and develops a slightly negative curvature as the temperature decreases. D-wave superconductors, at least the HTSC layered materials that are somewhat similar to the 2D organics [9], have a strong positive curvature [10][11]. Therefore, it is consistent to have a change in the slope of the H-T phase line if the superconductor changes the symmetry of its order parameter.

4. Conclusions

We have found a second organic conductor, BEDO, with an H-T phase line that has a distinctive positive change of its slope. Preliminary data in BETS, the first organic salt where this type of phase diagram was seen, shows a kink in the $H_{C2\parallel}$ line at the same temperature. The kink in both salts could be magnetic in origin, although it is more consistent with a change in the superconducting order parameter.

5. References

[1] R. H. McKenzie, Science **278**, 820 (1997). *Organic Superconductors*, J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M-H. Whangbo, Prentice Hall (1992).

[2] S. Belin and K. Behnia, Phys Rev. Lett. **79**, 2125 (1997).

[3] C. H. Mielke, C. C. Agosta, S. A. Ivanov, D. A. Howe, L. K. Montgomery, and G. Athas, and R. Movshovich submitted to *Phys. Rev. Lett.*

[4] S. T. Ruggiero, T. W. Barbee, Jr. and M. R. Beasley, Phys. Rev. Lett. **45**, 1299, (1980).

[5] L. N. Bulaevskii and O. V. Dolgov, *JETP Lett.*, **45**, 526 (1987).

[6] S. Ivanov, T. Coffey, C. C. Agosta, S. T. Hannahs, C. Immer, N. D. Kushch and E. B. Yagubskii, *Synth. Metals.* **85**, 1499 (1997).

[7] M. B. Maple, H. C. Hamaker and L. D. Woolf, Chap 4 of Superconductivity in Ternary Compounds II, M. B. Maple and O. Fischer eds. Topics in Current Physics, Vol. 34 (Springer, Berlin, 1982).

[8] G.Bruls, D. Weber, B. Wolf, P. Thalmeier, and B. Lüthi, *Phys. Rev. Lett.* **65**, 2294 (1990).

[9] K. Murata, Y. Honda, H. Anzai, M. Tokumoto, K. Takahashi, N. Kinoshita, T. Ishiguro, N. Toyota, T. Sasaki, and Y. Muto, Synth. Met. **27**, A341 (1988).

[10] A. P. Mackenzie, S. R. Julian, G. G. Lonzarich, A. Carrington, S. D. Hughes, R. S. Liuadn D. C. Sinclair, *Phys. Rev. Lett.* **71**, 1238 (1993).

[11] M. S. Osofsky, R. J. Soulen, Jr., S. A. Wolf, J. M. Broto, H. Rakoto, J. C. Ousset, G. Coffe, S. Askenazy, P. Pari, I. Bozovic, J. N. Eckstein, and G. F. Virshup, *Phys. Rev. Lett.* **71**, 2315 (1993).