PHYSICAL REVIEW B VOLUME 42, NUMBER 16 1 DECEMBER 1990

Specific heat in zero and applied magnetic fields of the organic superconductor α-di[bis(ethylenedithio)tetrathiafulvalene]-ammonium-tetra(thiocyanato)mercurate [α-$(ET)_2(NH_4)Hg(SCN)_4$]

B. Andraka and G. R. Stewart*
Department of Physics, University of Florida, Gainesville, Florida 32611

K. D. Carlson, H. H. Wang, M. D. Vashon, and J. M. Williams
Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439
(Received 19 April 1990)

Specific heats determined down to 0.3 K establish the existence of bulk superconductivity in a new α-phase superconducting salt, α-di[bis(ethylenedithio)tetrathiafulvalene]-ammonium-tetra(thiocyanato)mercurate [α-$(ET)_2(NH_4)Hg(SCN)_4$] ($T_c = 1$ K), a derivative of the organic radical-cation donor molecule bis(ethylenedithio)tetrathiafulvalene (ET). This salt is important because it establishes a new structural class of organic superconductors, the α-phase class. The anomaly in the specific heat C is distinct but broad with a maximum in C/T at 0.8 K. The measurements yield a normal-state Sommerfield coefficient of $\gamma = 29\pm2$ mJ/K^2 mol, which is essentially identical to those of other ET-based organic superconductors, and an approximate value $\Delta C/\gamma T_c = 1.1\pm0.2$, which is smaller than the BCS value of 1.43. A sharp but unexplained increase in C/T occurs below 0.7 K. Determinations of the temperature derivatives of the upper critical magnetic fields at $T_c(-dH_{c2}/dT)$, from specific heats measured in applied magnetic fields, yield an extremely large value larger than 3 T/K for $\mathbf{H}\parallel ac$, where ac denotes the crystallographic ac plane (which contains the tightly connected conducting layers of ET donor molecules), and a value of 0.1 ± 0.02 T/K for $\mathbf{H}\parallel b^*$.

INTRODUCTION

Research in organic superconductors is motivated by a steady pace of increasing superconducting transition temperatures T_c and by the highly anisotropic and frequently unusual properties exhibited by these novel materials. These studies are important in their own right, but in addition they eventually may have implications in understanding the similarly layered, high-T_c ceramic-oxide superconductors. Although there are now over 35 organic superconductors that have been reported since the discovery of organic superconductivity in 1979,[1] there are only a limited number of studies available that definitely established the existence of bulk superconductivity in these materials and that delineate the nature of the coupling mechanism and the superconducting energy gap.

Specific-heat measurements of organic superconductors near T_c have been reported to date only for the charge-transfer salts $(TMTSF)_2ClO_4$ (Ref. 2) (TMTSF represents the organic donor molecule tetramethyltetraselenafulvalene), β-$(ET)_2I_3$,[3] β-$(ET)_2AuI_2$,[4,5] and κ-$(ET)_2Cu(NCS)_2$ (Refs. 6–8) [ET represents the organic donor molecule bis(ethylenedithio)tetrathiafulvalene]. Recently, we have firmly established, by specific-heat measurements,[7] the existence of bulk superconductivity and evidence for strong-coupling superconductivity in the organic superconductor κ-$(ET)_2Cu(NCS)_2$, which possesses the third highest T_c ($=10.4$ K) (Ref. 9) after κ-$(ET)_2Cu[N(CN)_2]Br$ ($T_c = 11.6$ K) (Ref. 10) and κ-$(ET)_2Cu[N(CN)_2]Cl$ ($T_c = 12.8$ K, 0.3 kbar).[11] Herein we report on measurements of the specific heat near T_c in zero and applied magnetic fields of one of the newest superconducting charge-transfer salt of ET: α-$(ET)_2(NH_4)Hg(SCN)_4$. This salt was first synthesized by Oshima *et al.*,[12] but superconductivity, with an onset near 1.15 K and midpoint near 0.75 K, was discovered by Wang *et al.*[13] by the use of rf penetration-depth measurements. Despite its low T_c, α-$(ET)_2(NH_4)Hg(SCN)_4$, which possesses the donor molecule packing motif of *non*superconducting α-$(ET)_2I_3$,[14] is important because it establishes a new structural class of organic superconductors, the α-phase class.[13]

EXPERIMENT

Three single crystals with a total weight of 3.03 mg were attached to a sapphire platform by a small amount of thermally conductive Wakefield grease. The samples were aligned in such a way that the crystallographic b^* axis was normal to the platform. The orientation of the platform could be changed with respect to the applied magnetic field to achieve either $\mathbf{H}\parallel b^*$ or $\mathbf{H}\parallel ac$, where ac denotes the crystallographic ac plane, which contains the conducting donor-molecule layers. The temperature in the magnetic field was determined by the use of a 220-Ω, $\frac{1}{2}$-W Speer resistor calibrated in zero magnetic field against a Lake Shore Ge thermometer. Small magnetoresistance corrections for the Speer resistor were made following a procedure described by Naughton *et al.*[15]

Field values in our superconducting magnet have been checked by use of a Lake Shore transverse Hall probe. Addenda contributed about 50% of the total measured heat capacity at all temperatures. The specific heats were measured in the temperature range of 2.0–0.32 K. We estimate an absolute error of ±5–10 % in the specific-heat measurements.

RESULTS AND DISCUSSION

Plots of C/T, the specific heat C divided by the temperature T, versus T in zero and various applied magnetic fields H are illustrated in Fig. 1 for $\mathbf{H}\|b^*$ and in Fig. 2 for $\mathbf{H}\|ac$. One observes in these figures very distinct anomalies in C/T below 1 K, which are suppressed by increasing magnetic field strengths, and an unusual upturn in C/T below 0.7 K. At temperatures above 1 K, the specific heat has the usual normal-state temperature dependence $C/T=\gamma+\beta T^2$. From a least-squares analysis, we obtain the electronic coefficient of specific heat $\gamma=29\pm2$ mJ/K^{2}mol and, from the β coefficient, a Debye temperature of 230±10 K. Because of the low temperatures, the lattice contribution is not excessively dominant, so that γ is determined fairly precisely by the least-squares analysis. Within the precision of the measurements, the Sommerfeld coefficient γ agrees with the values $\gamma=25\pm3$ mJ/K^{2}mol determined[7] for κ-(ET)$_2$Cu(NCS)$_2$ and $\gamma=24\pm3$ mJ/K^{2}mol determined[3] for β-(ET)$_2$I$_3$. Similarly, the Debye temperature is essentially the same as that of 215±10 K determined[7] for κ-(ET)$_2$Cu(NCS)$_2$ and close to the value of 197±5 K determined[3] for β-(ET)$_2$I$_3$. The Sommerfeld coefficient and Debye temperatures have not been determined from the specific heats of β-(ET)$_2$AuI$_2$,[4,5] but the data are at least consistent with $\gamma=24$ mJ/K^{2}mol.

The onset of superconductivity in α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ in zero applied field as determined from C/T is near 1.1 K, but the transition is very broad with a maximum in C/T occurring near 0.8 K. These values are in good agreement with the previously reported parameters of the superconducting transition determined from rf penetration-depth measurements.[13] The anomaly in the specific heat near T_c is suppressed by applied magnetic fields, and it appears to be totally suppressed at 900 Oe for $\mathbf{H}\|b^*$ (Fig. 1). Of considerable interest is the value of the discontinuity ΔC at T_c and the ratio $\Delta C/\gamma T_c$, which is a measure of the coupling strength. Because of the very broad distribution in T_c and the low-temperature upturn in C/T, however, we are unable to determine a precise value of $\Delta C/T_c$. We may obtain an estimate of the discontinuity by application of the equal-area construction method in which we replace the broad superconducting transition by an ideally sharp mean-field jump that conserves the total entropy. This method applied to the zero-field data yields $\Delta C/T_c=31.9$ mJ/K^{2}mol at $T_c=0.9$ K and a ratio $\Delta C/\gamma T_c=1.1\pm0.2$, which is smaller than the BCS ratio of 1.43. Although such ratios smaller than the BCS value are known to occur for several superconducting materials, e.g., the ratios for zinc and thallium are 1.25 and 1.15, respectively,[16] the uncertainty in our present estimate is sufficiently large that we cannot conclude anything definite at this time on the coupling strength in superconducting α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$. In the case of κ-(ET)$_2$Cu(NCS)$_2$, we were able to obtain a reliable value of $\Delta C/\gamma T_c>2$ and thus evidence for strong-coupling superconductivity.[7]

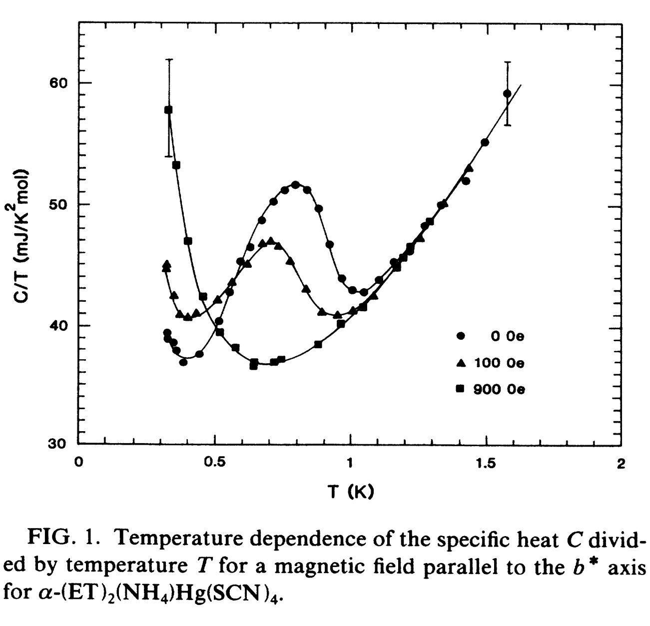

FIG. 1. Temperature dependence of the specific heat C divided by temperature T for a magnetic field parallel to the b^* axis for α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$.

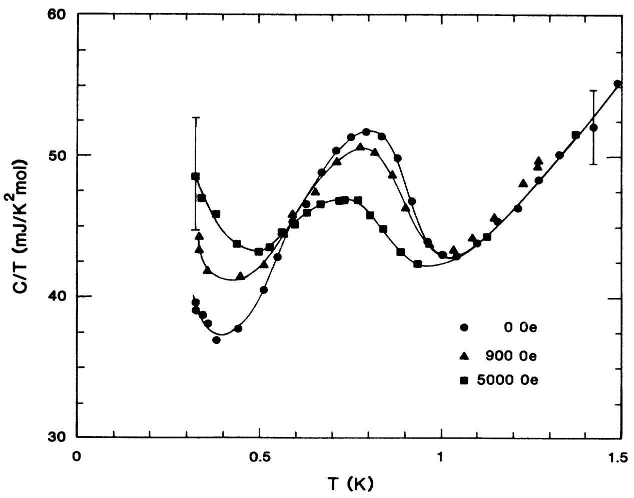

FIG. 2. Temperature dependence of the specific heat divided by temperature for a magnetic field parallel to the ac plane for α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$.

With T_c defined as the temperature at the maximum in C/T, we find that a magnetic field of 100 Oe suppresses T_c by 0.1±0.02 K for $\mathbf{H}\|b^*$ (Fig. 1). Thus, the temperature derivative of the upper critical magnetic field, evaluated at T_c, for this field direction is $-(dH_{c2}/dT)_{T_c}=0.1\pm0.02$ T/K. For $\mathbf{H}\|ac$, a field of 900 Oe suppresses T_c by 0.02±0.01 K and a field of 5 kOe suppresses T_c by 0.06±0.02 K (Fig. 2). These values yield a very high initial slope for this latter field direction, larger than 3 T/K. This slope is at least two times larger than those determined from magnetoresistance measurements for all other organic superconductors, except the high-pressure superconductor[17] β^*-$(ET)_2I_3$ [$T_c = 7.5$ K, $-(dH_{c2}/dT)_{T_c} = 4.8$ T/K for $H \| ab$]. Furthermore, the anisotropy ratio of 25:1 or larger exceeds those reported for all other organic superconductors: e.g., β-$(ET)_2I_3$ ($T_c \cong 1.1$ K), 22:1;[18] β^*-$(ET)_2I_3$ ($T_c \cong 7.5$ K), 12:1,[17] β-$(ET)_2AuI_2$ ($T_c \simeq 4.0$ K), 13:1,[19] $(ET)_4Hg_{2.89}Br_8$ ($T_c \cong 4.3$ K), 20:1;[20] and κ-$(ET)_2Cu(NCS)_2$ ($T_c \cong 10.4$ K), 19:1.[8] However, we would like to stress that, because of the broadness of the superconducting transition, the difficulty in defining a precise T_c, and the limited number of fields for which specific-heat data were taken, there is considerable uncertainty in the values of the present slopes, especially for the high-field direction where the temperature intervals are very small. For the same reasons, the curvature for low $H \| ac$ is not discernible. Thus, further measurements of $H_{c2}(T)$ by other methods are required to establish precise temperature dependencies. [It should be noted that recent specific-heat determinations of the initial slopes of $H_{c2}(T)$ for the κ-$(ET)_2Cu(NCS)_2$ superconductor have yielded much larger values than those determined from resistive measurements.][8]

We have no convincing explanation for the origin of the upturn in C/T below 0.7 K. The excess of the low-temperature specific heat in a field of 900 Oe compared to the extrapolated zero-field normal-state specific heat can be well described by a $1/T^2$ dependence. Such behavior is observed on the high-temperature side of a Schottky anomaly. A similar upturn is observed in C measured in a field of 5 T, but this is not shown in Fig. 1 for clarity. One judges from the magnitude of C/T in this low-temperature region that the upturn is not likely to be associated with a minor impurity.

In summary, our measurements of the specific heat definitely establish the existence of bulk superconductivity in α-$(ET)_2(NH_4)Hg(SCN)_4$ with $T_c = 0.8$ K and indicate the development of a superconducting energy gap in the electronic density-of-states spectrum. Because the superconducting transition of the ensemble of three crystals is very broad, indicating an inhomogeneous distribution in T_c, we are unable to determine an unequivocal measure of the coupling strength through the ratio $\Delta C/\gamma T_c$. Our determination of γ indicates that it is essentially the same value as those currently available for other ET-based superconducting salts. This is a significant observation in consideration of the range of T_c's from $T_c < 1$ K to $T_c > 10$ K: the constancy of γ, which is proportional to the electronic density of states, implies that T_c for these superconductors is determined primarily by changes in the coupling strength, as has been suggested previously[21] for the isostructural class of β-phase superconductors, β-$(ET)_2X$, $X = I_3^-$, IBr_2^-, AuI_2^-, and β^*-$(ET)_2I_3$. The temperature derivatives of $H_{c2}(T)$ at T_c in the high-field direction appears to be much larger than those reported for most other organic superconductors, and the anisotropy ratio of the critical magnetic fields also seems to be exceptionally large. Finally, the specific-heat measurements indicate the occurrence of some unusual but as yet unexplained anomaly for $T < 0.7$ K which leads to a large increase in C/T.

ACKNOWLEDGMENTS

Work at the University of Florida and Argonne National Laboratory was performed under the auspices of U.S. Department of Energy, Office of Basic Energy Sciences, Division of Material Sciences, Grant No. DE-FG05-86ER45268 and Contract No. W-31-109-ENG-38, respectively. M.D.V. acknowledges partial financial support from the Argonne Division of Educational Programs.

---

*Also at University of Augsburg, Germany.

[1] D. Jérome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. (Paris) Lett. **41**, L95 (1980).

[2] P. Garoche, R. Brusetti, D. Jérome, and K. Bechgaard, J. Phys. (Paris) Lett. **43**, L147 (1982); R. Brusetti, P. Garoche, and K. Bechgaard, J. Phys. C **16**, 3535 (1983).

[3] G. R. Stewart, J. O'Rourke, G. W. Crabtree, K. D. Carlson, H. H. Wang, J. M. Williams, F. Gross, and K. Andres, Phys. Rev. B **33**, 2046 (1985).

[4] G. R. Stewart, J. M. Williams, H. H. Wang, L. N. Hall, M. T. Perozzo, and K D. Carlson, Phys. Rev. B **34**, 6509 (1986).

[5] K. Andres, H. Schwenk, and H. Vieth, Physica B **143**, 334 (1986).

[6] S. Katsumoto, S. Kobayashi, H. Urayama, H. Yamochi, and G. Saito, J. Phys. Soc. Jpn. **57**, 3672 (1988).

[7] B. Andraka, J. S. Kim, G. R. Stewart, K. D. Carlson, H. H. Wang, and J. M. Williams, Phys. Rev. B **40**, 11 345 (1989).

[8] J. E. Graebner, R. C. Haddon, S. V. Chichester, and S. H. Glarum, Phys. Rev. B **41**, 4808 (1990).

[9] H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kanamoto, and J. Tanaka, Chem. Lett. p. 55 (1988).

[10] A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung, M.-H. Whanbgo, Inorg. Chem. **29**, 2555 (1990).

[11] J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. Streiby Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung, and M.-H. Whangbo, Inorg. Chem. **29**, 3272 (1990).

[12] M. Oshima, H. Mori, S. Saito, and K. Oshima, Chem. Lett. p. 1159 (1989); M. Oshima, H. Mori, G. Saito, and K. Oshima (unpublished).

[13] H. H. Wang, K. D. Carlson, U. Geiser, W. K. Kwok, M. D. Vashon, J. E. Thompson, N. F. Larsen, G. D. McCabe, R. S. Hulscher, and J. M. Williams, Physica C **166**, 57 (1990).

[14] K. Bender, K. Dietz, H. Endres, H. W. Helberg, I. Hennig, H. J. Keller, H. W. Schaefer, and D. Schweitzer, Mol. Cryst. Liq. Cryst. **107**, 45 (1984).

[15] M. J. Naughton, S. Dickinson, R. C. Samaratunga, J. S. Brooks, and K. P. Martin, Rev. Sci. Instrum. **54**, 1529 (1983).

[16] J. Bardeen and J. R. Schrieffer, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience, New York,

1961), Vol. 3, p. 212.

[17] L. N. Bulaevskii, V. B. Ginodman, and A. V. Gudenko, Pis'ma Zh. Eksp. Teor. Fiz. **45**, 355 (1987) [JETP Lett. **45**, 451 (1987)].

[18] M. Tokumoto, H. Bando, H. Anzai, G. Salto, K. Murata, K. Kajimura, and T. Ishiguro, J. Phys. Soc. Jpn. **54**, 869 (1985).

[19] H. Schwenk, S. S. P. Parkin, V. Y. Lee, and R. L. Greene, Phys. Rev. B **34**, 3156 (1986).

[20] R. N. Lubovskaya, E. I. Zhilyaeva, S. I. Pesotskii, R. B. Lubovskii, L. O. Atovmyan, O. A. D'Yachenko, and T. G. Takhirov, Pis'ma Zh. Eksp. Teor. Fiz. **46**, 149 (1987) [JETP Lett. **46**, 188 (1987)].

[21] M.-H. Whangbo, J. M. Williams, A. J. Schultz, T. J. Emge, and M. A. Beno, J. Am. Chem. Soc. **109**, 90 (1987).