PHYSICAL REVIEW B VOLUME 51, NUMBER 5 1 FEBRUARY 1995-I

# Anomalous vortex dynamics in $\kappa$-[bis(ethylenedithio)tetrathiafulvalene]$_2$Cu[N(CN)$_2$]Br: Evidence for field-induced magnetic order and unconventional superconductivity

U. G. L. Lahaise, Qun Chen, and L. E. De Long*
*Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055*

C. P. Brock
*Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055*

H. H. Wang, K. D. Carlson, J. A. Schlueter, and J. M. Williams
*Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439*
(Received 21 July 1994; revised manuscript received 31 October 1994)

Anisotropic superconducting flux-line behavior of single-crystal $\kappa$-[bis(ethylenedithio)tetrathiafulvalene]$_2$Cu[N(CN)$_2$]Br has been studied with dc magnetization and vibrating-reed (VR) techniques. A peak at $T^*(H)$ in the temperature dependence of the VR inverse quality factor $1/Q$ exhibits a shoulder for magnetic fields $0<\mu_0 H \leq 0.5$ T parallel to the conducting ac plane. The shoulder becomes unresolved near a kink in $T^*(H)$ at $\mu_0 H \approx 0.7$ T. Discontinuities in $1/Q$ and the VR frequency shift occur for $0.1 \leq \mu_0 H \leq 1.3$ T applied perpendicular to the ac plane and temperatures $T \leq 20$ K, well into the normal state. These anomalies are preliminary evidence for a field-induced magnetic phase transition and unconventional superconductivity.

Layered organic superconductors continue to be a subject of intense interest since their perpendicular coherence length can be a factor of 3 or 4 less than the separation between conducting layers of organic donor molecules, leading to nearly two-dimensional superconducting behavior.[1] $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br [ET is bis(ethylenedithio)tetrathiafulvalene] is particularly intriguing since it has a high superconducting transition temperature $T_c \approx 11.6$ K,[2] and exhibits a very unusual temperature dependence of the upper critical magnetic field $H_{c2}(T)$.[3]

Anomalous curvature or kinks in $H_{c2}(T)$ can be a signature of unconventional (e.g., $p$- or $d$-wave) pairing,[4,5] especially in materials exhibiting competition between magnetic and superconducting ground states.[4–6] On the other hand, they may be caused by anomalous flux line (FL) dynamics,[7] as evidenced by the "vortex lock-in transition" (i.e., abrupt alignment of the magnetic induction parallel to the conducting ac planes) recently observed for $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br.[8,9] The relative importance of these two mechanisms for the unusual properties of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br remains controversial.[6]

We have investigated $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br by use of the vibrating-reed (VR) technique, which is a powerful probe of FL dynamics, involving measurement of the flexural oscillations of a thin rectangular reed clamped at one end in cantilever geometry.[7,10,11] When a vibrating reed is loaded on its free end with a superconducting sample and is subjected to applied magnetic fields, diamagnetic surface currents flowing in the sample produce a magnetic restoring force that leads to an increase $\Delta f$ in the resonant frequency $f$ compared to its normal state value $f_0$ with decreasing temperature (see Fig. 1). A maximum in dissipation ($\approx$ inverse quality factor $1/Q$) is usually observed at temperatures and fields near or below $H_{c2}(T)$.[10] The $\Delta f/f$ and $1/Q$ anomalies can be explained[7,10] as characteristics of a boundary ("depinning line") between mobile and immobile ("pinned") regimes of FL behavior, although their precise origin (e.g., FL lattice melting vs depinning) remains controversial.[7,12,13]

Four samples of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br used in this work were prepared by electrocrystallization techniques described elsewhere;[14,15] representative data for two samples ("B" and "F") will be presented here. X-ray-diffraction data indicated that sample B was an orthorhombic single crystal with lattice parameters $a=12.932(2)$, $b=29.938(4)$, and $c=8.529(1)$ Å, whose major faces were {010} and {101}, where the {010} faces are parallel to the ac plane. Sample F was of polycrystalline structure, but VR and structural data indicate that it was highly aligned along the **b** direction.

Each sample (thin plate of mm dimensions) was mounted on a single-crystal Si reed (dimensions $\approx 1$ cm$\times 1$ mm $\times 80$ $\mu$m) by use of Apiezon vacuum grease.[11,12] The sample conducting ac plane was fixed parallel to the reed axis, which was either parallel ("longitudinal"; see inset of Fig. 3) or perpendicular ("transverse"; see inset of Fig. 4) to the applied dc magnetic field.[12,13] The superconducting properties of samples B and F (and two other crystals not described here) were found to be reproducible and very similar, although a small VR signal precluded the acquisition of good data for sample B in the transverse geometry. dc magnetization measurements were performed on sample F in a transverse orientation using a vibrating sample magnetometer. The first penetration field $H_p(T)$ ($\leq H_{c1}$, the lower critical field) was determined as the field for first deviation from a linear diamagnetic magnetization $M$ vs $H$, starting from a zero-field-cooled state. $H_{c2}(T)$ was determined from a marked change in slope in $M$ vs $T$ after zero-field cooling and the application of a modest transverse field.[3] The irreversibility line $H_{\rm irr}(T)$ was determined from the onset field of hysteresis in isothermal magnetization curves.

Longitudinal VR data for both samples exhibit a "high-field regime" (Fig. 1, top), and a "low-field regime" (Fig. 1,

 

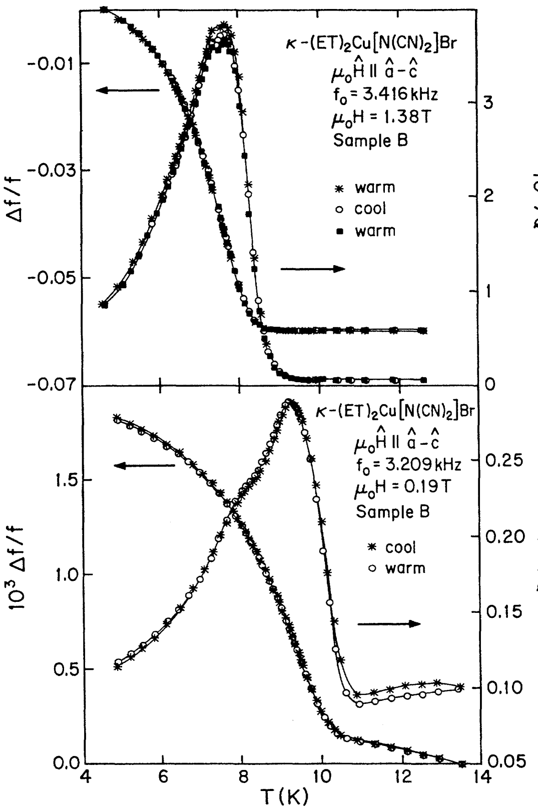


FIG. 1. "High-field" (top: $\mu_0 H = 1.38$ T) and "low-field" (bottom: $\mu_0 H = 0.19$ T) data for the relative frequency shift $\Delta f/f$ and the inverse quality factor $1/Q$ versus temperature $T$ for sample B in the longitudinal geometry.

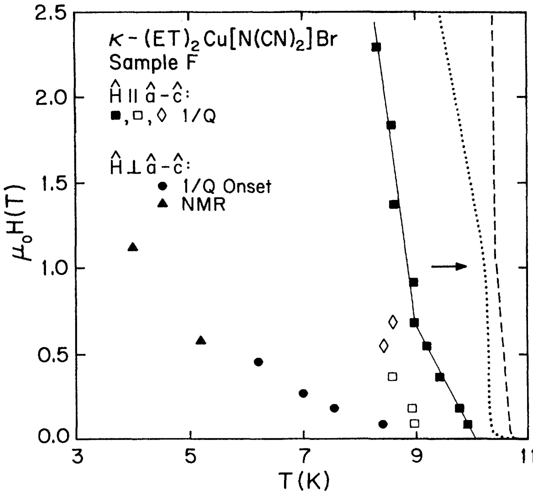


FIG. 2. Main peak at $T^*(H)$ (solid squares), corresponding shoulder (open squares), and marginally resolved shoulder (open diamonds) in inverse quality factor $1/Q$ for temperature ($T$) sweeps for sample F in the longitudinal geometry. The onset of the $1/Q$ anomaly and the NMR relaxation peaks (Refs. 9 and 27) are shown for the transverse geometry. The dashed and dotted lines denote $H_{c2}(T)$ (Ref. 3) in the longitudinal and transverse geometries, respectively. Kinks in $\mu_0 H_{c2}(T)$ near 1 T are marked by the arrow. The solid line is a guide to the eye.

bottom). A distinct, reproducible shoulder is present on the low-temperature side of the low-field dissipation peaks. The shoulder either vanishes or becomes unresolved near temperatures and fields where a pronounced change in slope or "kink" appears in $T^*(H)$, defined as the position of the main dissipation peak in the $H$-$T$ diagram, shown in Fig. 2.

The kink in $T^*(H)$ is qualitatively similar to an abrupt change in the slope of $H_{c2}(T)$ at $\mu_0 H \approx 1$ T (at $T = T_c > T^*$), as observed in dc magnetization measurements;[3] moreover, our data demonstrate that there is important structure in the $H$-$T$ phase diagram below $H_{c2}$ that has not been detected previously for $\kappa$-$(ET)_2Cu[N(CN)_2]Br$. The anisotropy ratio $R = H_{\parallel}/H_{\perp}$ for $H_{c2}$ measured[3] for applied field parallel and perpendicular to the conducting plane, respectively, increases by a factor of $\sim 6$ as $\mu_0 H_{c2}$ increases through 1 T, which Kwok *et al.* attribute to a transition from anisotropic, three-dimensional, bulk superconductivity to two-dimensional, Josephson-coupled superconductivity. Assuming Kwok *et al.* measured the true equilibrium phase boundary ($H_{c2}$), the similarity between the character and field values of the kinks in $\mu_0 H_{c2} \approx 1$ T (see Ref. 3 for details) and $T^*$ ($\mu_0 H \approx 0.7$ T) suggest that the latter is not a simple consequence of FL pinning or diffusion (generally dominated by sample size and defects), but may signal a new phase transition.

Double dissipation peaks have been observed in conventional,[13,16–18] as well as organic and high-$T_c$ superconductors,[19,20] where they were attributed to anisotropic flux-line diffusion modes[21] or the successive decoupling and melting of two-dimensional, "pancake" vortices.[22] However, shoulders or double peaks in $1/Q$ vs $T$ may also indicate a mixture of two superconducting phases present in our samples. In particular, the $T_c$ of $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ is reduced by approximately 1 K by rapid cooling, possibly due to incomplete ordering of the ethylene groups,[3] or as a consequence of small stresses induced by mounting samples with insulating varnish or vacuum grease.[15] A phase mixture could also result if phase transitions reported[23,24] near 20 and 80 K are incomplete.

We have performed field-sweep experiments in the longitudinal geometry to determine if the higher-temperature $1/Q$ *crosses* the shoulder at the kink in $T^*(H)$, which would be evidence for a spatially segregated phase mixture exhibiting two independent $T_c$'s and $H_{c2}$ phase boundaries. The main dissipation peak in field-sweep data occurs at a point $H^*(T)$ consistent with the temperature-sweep peaks at $T^*(H)$, as shown in Figs. 1–3 (the large width of the main peak could hide another anomaly corresponding to the shoulder in the temperature sweep data). A reproducible second anomaly is present on the high-field side of the dissipation peak, but its location in the $H$-$T$ phase diagram places it at fields approaching $H_{c2}(T)$. Note that the second dissipative anomaly measured in field sweeps is accompanied by a corresponding second anomaly in frequency shift (Fig. 3), which is not observed in temperature sweep data (Fig. 1). We cannot entirely rule out crossing $T^*$ anomalies derived from spatially distinct regions of the samples *if* unusually large hysteresis ($T$ vs $H$) effects are present in our measurements *and* the higher-field anomaly is not a signature of $H_{c2}$.

Temperature sweeps carried out in the longitudinal geom-

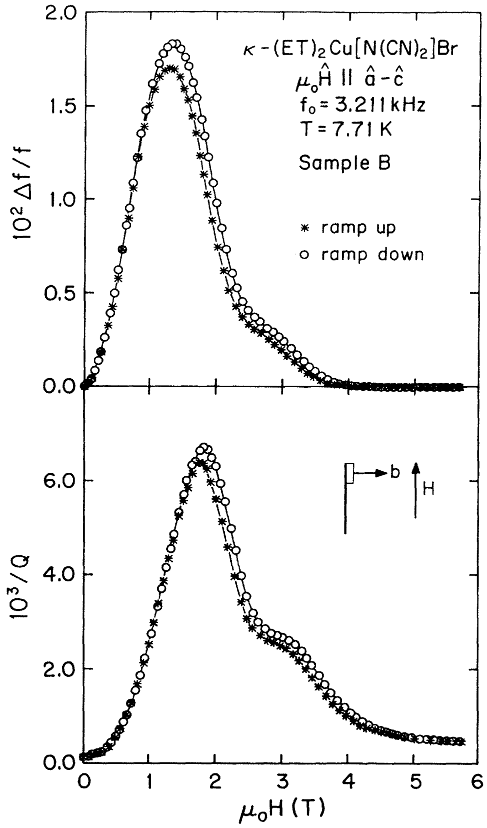


FIG. 3. Relative frequency shift $\Delta f/f$ and inverse quality factor $1/Q$ versus magnetic field $H$ for sample B in the longitudinal geometry (see lower inset) at $T=7.71$ K.

etry in the low-field (Fig. 1, bottom) and high-field (Fig. 1, top) regimes revealed no measurable temperature hysteresis below $T^*(H)$. A longitudinal reed exhibited no measurable field hysteresis below the peak in $1/Q$, defining $H^*(T)$,

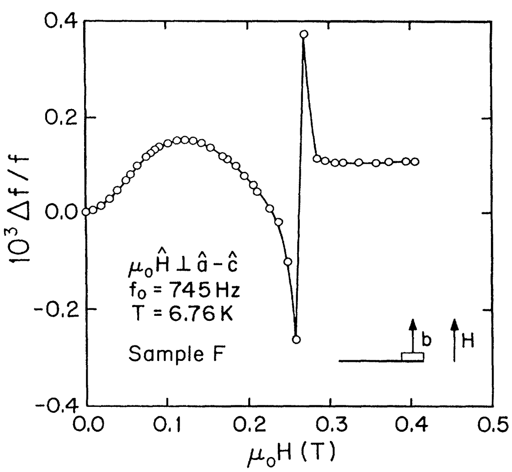


FIG. 4. Relative frequency shift $\Delta f/f$ and inverse quality factor $1/Q$ versus magnetic field $\mu_0 H$ for sample F in the transverse orientation (see inset) at $T=6.76$ K. The line is a guide to illustrate a discontinuity.

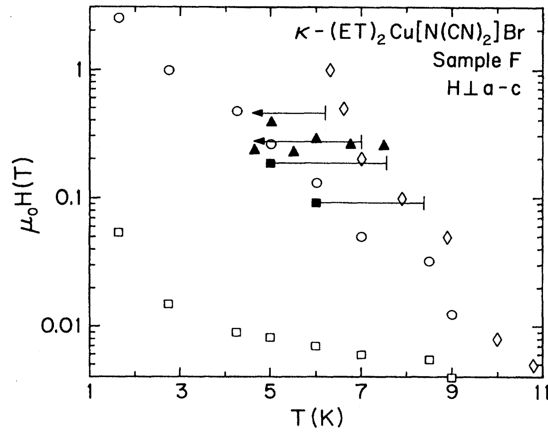


FIG. 5. Magnetic field $H$ versus temperature $T$ phase diagram for sample F in a transverse orientation. The open diamonds, squares, and circles denote the upper critical magnetic field $H_{c2}$, first penetration field $H_p$, and irreversibility line $H_{\mathrm{irr}}$, respectively, from dc magnetization measurements. Resolved peaks (solid squares), discontinuities (solid triangles), onsets (vertical bars), and low-temperature limits (arrows) are shown for anomalies in the VR inverse quality factor $1/Q$.

while some hysteresis is detected in $1/Q$ above $H^*$, and in $\Delta f/f$ at $H>1$ T (Fig. 3). This high-field hysteresis is in contrast to measurements of other materials interpreted with vortex diffusion models[7,10] (which would generally predict low-field hysteresis below $H^*$), and could indicate a field-induced phase transition near $H^*$.

The possibility of a magnetic phase transition is reinforced by observations of a discontinuity in $\Delta f/f$ and $1/Q$ for both samples in field sweeps performed in the transverse geometry, as shown in Fig. 4. We did not observe the discontinuity in any measurement taken in the longitudinal geometry or in temperature sweeps, but found it to persist from 4 K to at least 20 K (above $T_c$), precluding its explanation as a vortex pinning anomaly. We performed several VR and magnetic-susceptibility measurements on the empty Si reeds, vacuum grease, and piezo transducers used in this study to rule out a spurious origin of the discontinuity.

The discontinuity could be due to a field-induced magnetic transition, such as the predicted[25] "field-induced spin-density wave," occurring when a magnetic field applied perpendicular to the conducting plane (i.e., our transverse geometry) provides a sufficient increase in anisotropy. Thermal expansion anomalies at ~80 K and ~20 K have been observed by Kund *et al.*,[23] which could indicate the development of a density wave or weak magnetic order at zero applied field. Welp *et al.*[26] reported an antiferromagnetic transition near 45 K and a weakly ferromagnetic state below 22 K which seems spatially mixed with stress-sensitive superconducting regions below $T_c \approx 12.6$ K for $\kappa$-$(ET)_2Cu[N(CN)_2]Cl$. Reentrant superconductivity in the presence of magnetic order also has been detected in the Cl material at very low applied pressures.[6] Therefore, $\kappa$-$(ET)_2Cu[N(CN)_2]Br$ might also be expected to have a mixture of normal and superconducting domains below 11 K, whose extent is stress dependent and thermally hysteretic. The threshold fields (0.1–1.3 T) of the discontinuities are sample dependent and nearly independent of temperature (see Fig. 5). Some scatter in the data might result from a hysteretic reconfiguration of normal and superconducting domains in samples warmed above the phase transitions at 20 and 80 K between experiments.

The anomalies in $\Delta f/f$ and $1/Q$ are broad in the transverse geometry, reflecting the shallow slope of $T^*(H)$ in this orientation. Vibrating-reed and dc (zero-field-cooled) magnetization data taken for the same sample reveal that the dissipation line $T^*(H)$ lies well below $H_{c2}(T)$, demonstrating that an extended region of reversibility with highly mobile vortices exists above $T^*(H)$, as shown in Fig. 5. The large discrepancy between our $H_{c2}(T)$ data and those of Kwok *et al.*[3] (Fig. 2) for different samples is not presently understood; however, it may be related to the short $b$-lattice parameter (0.08 Å samller than published values[1]) measured for sample B.

The $T^*(H)$ line traced out by the VR dissipation peaks lies very close to published anomalies in NMR relaxation rate $T_1^{-1}$ (Refs. 9 and 27) (see Fig. 2), which were tentatively attributed to local field fluctuations induced by vortex dynamics. Our VR data are strong evidence that the NMR and VR data are indeed caused by the same vortex behavior. However, a puzzle remains concerning the agreement between the NMR and VR data for $T^*(H)$ for $\mathbf{H}\|b$, given the very different time scales sampled in the NMR ($10^7-10^8$ Hz) and VR ($10^2-10^3$ Hz) experiments. The apparent lack of frequency dependence of the transverse dissipation anomalies casts doubt on the existence of a simple FL diffusion mechanism[7] acting over a range of hopping time scales.

We note that the first penetration field $H_p(T)$ inferred from zero-field-cooled dc magnetization data in the *transverse* orientation (Fig. 5), and the *transverse* $H_{c2}(T)$ data of Kwok *et al.*[3] (Fig. 3) both appear to exhibit an abrupt change in slope, and suggest that the kink in longitudinal $T^*$ and $H_{c2}(T)$ data are not a consequence of a FL lock-in effect (which is an artifact of the *longitudinal* orientation). We propose that the opposite curvatures of the transverse and longitudinal $H_{c2}$ data of Kwok *et al.* and the abrupt increase in $R$ for $H \approx 0.7$ T are evidence for the onset of strong, anisotropic Pauli limiting[4] behavior for $\mathbf{H}\|b$ due to the onset of a field-induced magnetic state for $H>1$ T. Furthermore, such $H_{c2}(T)$ behavior, the kink in $T^*(H)$, the field-induced transition, and the strain sensitivity of the superconducting properties constitute evidence for a unconventional superconducting order parameter, since they correspond to similar characteristics of the heavy-fermion superconductor $UPt_3$.[4,5]

The authors wish to thank Efrain Figueroa for assistance in magnetometer measurements, and Professor J. W. Brill, Dr. R. A. Klemm, Professor L. K. Montgomery, Dr. M. R. Norman, and Professor J. Sauls for useful discussions. Research at the University of Kentucky was supported by NSF Grant No. EHR-9108764. Research at the Argonne National Laboratory was supported by U.S. DOE Contract No. W-31-109-ENG-38.

*Author to whom correspondence should be sent.

[1] J. M. Williams *et al.*, Science **252**, 1501 (1991).
[2] A. M. Kini *et al.*, Inorg. Chem. **29**, 2555 (1990).
[3] W. K. Kwok *et al.*, Phys. Rev. B **42**, 8686 (1990).
[4] J. A. Sauls, Adv. Phys. **43**, 113 (1994).
[5] H. v. Löhneysen, Physica B **197**, 551 (1994).
[6] T. Ishiguro *et al.*, J. Supercond. **7**, 657 (1994).
[7] E. H. Brandt, J. Alloys Compounds **181**, 339 (1992).
[8] F. Steinmeyer, R. Kleiner, P. Müller, and K. Winzer, LT-20 Proceedings [Physica B (to be published)].
[9] S. M. De Soto *et al.*, Phys. Rev. Lett. **70**, 2956 (1993).
[10] P. Esquinazi, J. Low Temp. Phys. **85**, 139 (1991).
[11] X.-D. Xiang J. W. Brill, and W. L. Fuqua, Rev. Sci. Instrum. **60**, 3035 (1989).
[12] L. E. De Long, Z. G. Xu, J.-C. Hou, and J. Brill, in *Physical and Material Properties of High Temperature Superconductors*, edited by S. K. Malik and S. S. Shah (Nova Science, Commack, NY, 1994), pp. 383–407.
[13] H. Drulis *et al.*, Phys. Rev. B **44**, 4731 (1991).
[14] A. M. Kini *et al.*, Inorg. Chem. **29**, 2555 (1990).
[15] H. H. Wang *et al.*, J. Synth. Met. **41-43**, 1983 (1991).
[16] Z. Xu *et al.*, Physica C **202**, 2667 (1992).
[17] Z. Xu *et al.*, J. Phys. (France) IV, Colloq. **3**, C2-27 (1993).
[18] G. D'Anna *et al.*, Physica C **218**, 238 (1993).
[19] Y. Kopelevich *et al.*, Physica C **183**, 345 (1991); Y. Kopelevich, A. Gupta, and P. Esquinazi, Phys. Rev. Lett. **70**, 666 (1993).
[20] C. Duran *et al.*, Phys. Rev. B **44**, 7737 (1991).
[21] E. H. Brandt, Phys. Rev. Lett. **68**, 3769 (1992).
[22] J. R. Clem, Phys. Rev. B **43**, 7837 (1991).
[23] M. Kund *et al.*, Physica B **191**, 274 (1993).
[24] L. I. Buravov *et al.*, J. Phys. (France) I **2**, 1257 (1992).
[25] L. P. Gor'kov and A. G. Lebed', J. Phys. (Paris) Lett. **45**, 433 (1984).
[26] U. Welp *et al.*, Phys. Rev. Lett. **69**, 840 (1992).
[27] K. Kanoda *et al.*, Physica C **185-186**, 2667 (1991).