Fluctuation effects and mixed-state properties of the layered organic superconductors κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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We report on dc-magnetization measurements on high-quality single crystals of the organic superconductors κ-(BEDT-TTF)$_2$ Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br for fields parallel and perpendicular to the conducting planes. For H perpendicular to the planes, we find clear indications for strong superconducting fluctuations, i.e., a pronounced rounding of the transition with increasing field and field-induced diamagnetism above T_c. Careful experiments near T_c reveal the existence of a field-independent magnetization at $M^*(T^*,H)$ for $H \leq 10$ kOe. The anisotropy of superconducting parameters such as the upper critical field and coherence length, along with a scaling form of the high-field magnetization data demonstrate the highly anisotropic character for the present superconductors. Over an extended range in the H-T plane the mixed-state properties are governed by an entirely reversible vortex motion. The lower boundary of this range, the so-called irreversibility line, is found to be anisotropic and, for H perpendicular to the planes, to follow an exponential T dependence. Cooling below the irreversibility line is accompanied by the occurrence of magnetic relaxation effects, indicating a metastable vortex state.

I. INTRODUCTION

Organic superconductors among the charge-transfer salts of the κ-(BEDT-TTF)$_2X$ family [BEDT-TTF denotes bis(ethylenedithio)tetrathiafulvalene and X a monovalent anion] are characterized by a layered structure consisting of alternating sheets of metallic and insulating material. Conducting planes are formed by stacks of dimerized BEDT-TTF molecules via π-orbital overlap of sulfur (S) atoms of adjacent molecules. Since for the κ-phase salts the dimers are arranged in almost orthogonal order, the face-to-face (intradimer) overlap is of comparable size as the side-by-side (interdimer) overlap. This results in a two-dimensional S-S network of almost isotropic properties. The organic layers are separated by thin insulating sheets formed by the anions X. Owing to the layered crystal structure the electronic properties both above and below the superconducting transition are highly anisotropic. According to torque-magnetometry studies of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$,[1] this material has to be classified as a quasi-two-dimensional superconductor implying a mass anisotropy for the superconducting carriers moving perpendicular and parallel to the conducting planes of $\Gamma = m_\perp/m_\parallel = (\xi_\parallel/\xi_\perp)^2 \geq 4\times10^4 - 1.25\times10^5$, where $\xi_\parallel$ and $\xi_\perp$ are the coherence lengths parallel and perpendicular to the planes, respectively.

The reduced dimensionality along with other prominent characteristics of these superconductors such as a short coherence length, $\xi_\parallel \approx 20-60$ Å,[2-5] and a large in-plane magnetic penetration depth, $\lambda_\parallel \approx 5000-7000$ Å (Refs. 4 and 5) tend to enhance the effect of fluctuations of the order parameter. A measure of their strength is given by the Ginzburg number

$$G = |T - T_c|/T_c = \tfrac{1}{2}(k_B T_c)^2/(H_c^2(0)\xi_\parallel^2\xi_\perp)^2 ,$$

which relates the thermal energy to the condensation energy [$H_c(0)$ is the thermodynamic critical field] per coherence volume. For the present materials G is of the order of 10^{-2} which exceeds the values for conventional three-dimensional (3D) superconductors by several orders of magnitude. The temperature range $\Delta T = G\cdot T_c$, where critical fluctuations (fluctuations in the amplitude of the order parameter) occur, is believed to increase in a magnetic field.[6] The reason is that with increasing fields the confinement of the quasiparticles to low Landau orbits is accompanied by a further reduction of the effective dimensionality. Thus the pronounced field-induced broadening of the superconducting transition observed in both transport[1,7] and thermodynamic[3,8] measurements can be attributed to the effect of fluctuations. Superconducting parameters as the temperature dependence of the upper critical field H_{c_2} or the coherence length ξ extracted from these broadened transitions are subject to a substantial ambiguity depending on the measured quantity and the criterion used.

The special material parameters as the high anisotropy and the short coherence length do not only enhance the importance of fluctuations, they also affect the pinning properties in a way that pinning becomes weak. As a result, these superconductors disclose mixed-state properties which are unknown in conventional 3D materials. Magnetic measurements reveal an extended range in the H-T plane where vortices can move in an entirely reversible manner[4,5] accompanied by a large fluxoid dynamics.[9]

Resistive measurements demonstrate that in this state a dissipative mechanism is active which is different from a conventional Lorentz-force induced flux flow.[10]

The above phenomenology strongly resembles that of the layered oxide-based high-T_c superconductors. In fact, apart from the difference in their transition temperatures by one order of magnitude, these systems share a layered structure with a large value of the effective mass anisotropy, a short coherence length, and a large Ginzburg-Landau parameter κ.

In this paper we present dc-magnetization measurements on high-quality single crystals of the organic superconductors κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. In particular, we focus on effects related to the low dimensionality, i.e., the anomalous magnetic behavior close to the superconducting transition and in the mixed state. From an analysis of magnetization data at the superconducting transition we extract superconducting parameters as the upper critical field, the coherence length as well as their anisotropies. We look for scaling behavior of the high-field data, a property which has been proposed for anisotropic 3D and 2D superconductors. The lower boundary of the reversible range, the so-called irreversibility line, is mapped in the H-T plane. We also address its relation to the vortex dynamics as well as consequences on mixed-state derived parameters as the London penetration depth.

II. EXPERIMENTAL

The single crystals were grown by electrochemical oxidation as described elsewhere.[11,12] The crystals have platelike shapes with the largest face parallel to the planes of highest conductivity. Three crystals were selected weighing, respectively, 3.06 mg (No. 1) (No. 1 in Ref. 4), 0.4 mg (No. 2) for X=Cu(NCS)$_2$, and 2.48 mg (No. 3) (crystal described in Ref. 5) for X=Cu[N(CN)$_2$]Br. The dc-magnetization measurements were carried out with a commercial superconducting quantum interference device (SQUID) in fields up to 50 kOe. The crystals were attached to the sample holder by a small amount of Apiezon grease. Measurements were performed for two field configurations, i.e., the field aligned parallel and perpendicular to the conducting planes. A small misalignment within about 1° could not be excluded.

III. RESULTS AND DISCUSSION

A. Magnetic behavior around T_c

Figure 1 shows the magnetization data around the superconducting transition for the X=Cu(NCS)$_2$ [Fig. 1(a)] and X=Cu[N(CN)$_2$]Br [Fig. 1(b)] salts, respectively, measured in various fields perpendicular (left panels) and parallel (right panels) to the conducting planes. Both salts show a large diamagnetic normal-state magnetization (offset of each curve) which is of identical size for both field configurations and linear in the applied field. The corresponding susceptibilities of $\chi=-(3.48\pm0.1)10^{-4}$ emu/mol [X=Cu(NCS)$_2$] and $\chi=-(4.06\pm0.25)10^{-4}$ emu/mol [X=Cu[N(CN)$_2$]Br] are dominated by the large core contribution, a characteristic of these crystals containing large organic molecules. With increasing temperatures this diamagnetic background remains almost constant up to about 40 K above which a smooth increase becomes visible.

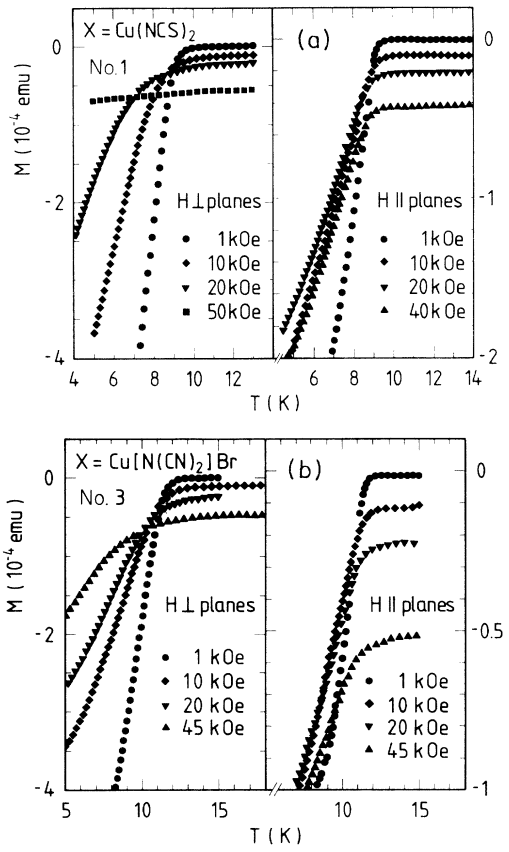

FIG. 1. Magnetization for various fields parallel (right panels) and perpendicular (left panels) to the conducting planes of κ-(BEDT-TTF)$_2X$ for (a) X=Cu(NCS)$_2$ and (b) X=Cu[N(CN)$_2$]Br.

Figures 1(a) and 1(b) clearly demonstrate the pronounced anisotropy for both materials. With increasing field applied perpendicular to the planes (left panels) the superconducting transition becomes considerably broadened with a shift of the diamagnetic onset to higher temperatures. In a field of H=10 kOe, for example, a careful analysis of the data (not shown) reveals a gradual growth of the diamagnetic signal starting at temperatures as high as $T\sim2\times T_c$ above which the signal is temperature independent within the resolution of our magnetometer. This field-induced contribution above the transition is accompanied with a decrease in the slope of the magnetization below. Both properties, which clearly distinguish these materials from three-dimensional superconductors, indicate the presence of strong superconducting fluctuations for this field configuration.

In contrast fields parallel to the planes [right panels of Figs. 1(a) and 1(b)] have only little effect on the superconducting transition. Its broadening is much less pronounced in particular for the X=Cu(NCS)$_2$ salt, where

the shape and the width of the transition remains essentially unaltered upon increasing the field. The rounding observed for the $X=Cu[N(CN)_2]Br$ salt might originate in a small misalignment from the exact $H\|$ planes configuration. For temperatures below the rather sharp transition the magnetization shows a linear behavior over an extended temperature range. The slope, dM/dT, decreases only slightly upon changing the field from 1 to 10 kOe, above which it remains nearly constant.

Before we turn to an analysis of the magnetic behavior we give more details of the transition for fields perpendicular to the planes. Figures 2(a) and 2(b) show the magnetization curves on expanded scales close to the superconducting transition for both salts in moderate fields $H \leq 10$ kOe. The data have been corrected for the T-independent diamagnetic normal-state magnetization. A peculiarity of both sets of data is the existence of a crossing point $M^*(T^*,H)$ at which the magnetization is field independent [we note that $M(T,H)$ data taken at fields $H \geq 20$ kOe do not meet M^*]. This unusual behavior, which has been observed also in high-quality single crystals of the high-T_c materials[13] has been attributed to the effect of superconducting fluctuations in quasi-two-dimensional superconductors. Two different sources of fluctuations have been considered. Bulaevskii, Ledvij, and Kogan have attributed the universal point to the effect of positional fluctuations of vortex pancakes in 2D superconductors for small fields $H_{crit} \approx \phi_0/(s^2\Gamma) \ll H \ll H_{c_2}(T^*)$.[14] On the other hand Tesanovic *et al.* consider amplitude fluctuations of the order parameter for higher fields $H > \frac{1}{3}H_{c_2}(T^*)$ as the origin of an universal point M^*.[15] In both models the universal point $M^*(T^*)$ is related to the effective interlayer distance s via $-M^*(T^*)=k_B T^*/(\phi_0 s)$, where correction factors of the order unity are neglected and ϕ_0 is the flux quantum. Applying this relation to the results of Figs. 2(a) and 2(b), where remarkably enough crossing is observed over a wide field range, we find $s=(75\pm5)$ Å and $s=(56\pm5)$ Å for the $X=Cu(NCS)_2$ and $X=Cu[N(CN)_2]Br$ salts, respectively. These values are much larger than the actual distance between the conducting layers (which most likely corresponds to the separation between the central TTF molecule in adjacent layers) of about 15 Å for both salts.[16] This discrepancy might indicate that at T^* the necessary condition $\xi_\perp \ll s$ is not satisfied and a strictly 2D model is not appropriate.[17]

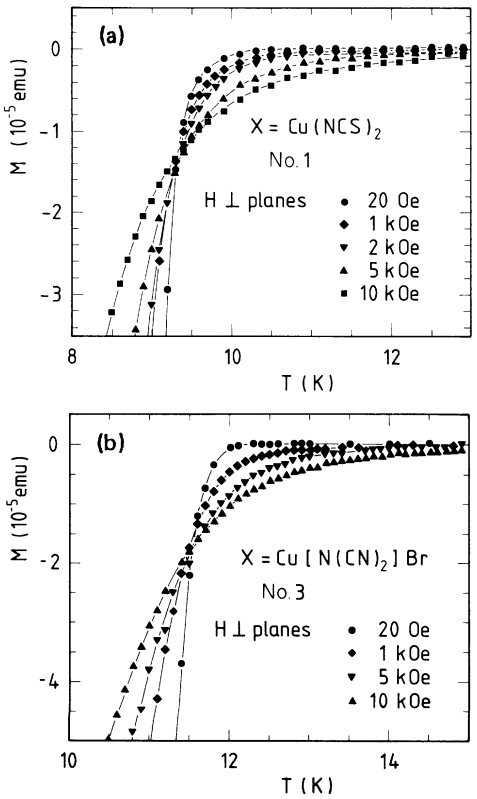

FIG. 2. Expanded view of magnetization curves for fields perpendicular to the conducting planes for (a) $X=Cu(NCS)_2$ and (b) $X=Cu[N(CN)_2]Br$. The data have been corrected for a T-independent background.

B. Scaling behavior

Figures 1 and 2 demonstrate that with increasing strength of fluctuations the transition into the superconducting state becomes increasingly undefined. As mentioned above the assertion of a mean-field transition temperature, $T_c^{mf}(H)$, under these conditions is not evident. The effect of fluctuations on transport and thermodynamic properties has been studied for classical layered superconductors[18] and, more extensively, for the high-T_c materials. For the latter, various methods have been used to determine $T_c^{mf}(H)$ depending on the dimensionality and the field- and temperature range investigated. One line of analysis follows the calculations of Ullah and Dorsey[19] based on the Lawrence-Doniach model.[20] For magnetic fields high enough so that the quasiparticles can be thought of to be in their lowest Landau levels, the authors predict a scaling behavior for various transport and thermodynamic properties. For the magnetization a scaling form of $M/(TH)^n=F\{A[T-T_c(H)]/(TH)^n\}$ is expected, where F is a scaling function, A a temperature- and field-independent coefficient, and $n=\frac{2}{3}$ for anisotropic 3D materials and $n=\frac{1}{2}$ for a 2D system. This procedure is supposed to allow for a determination of both the prevailing dimensionality as well as the mean-field transition temperature $T_c^{mf}(H)$. The high-field limit nominally requires that for a given field H the scaling behavior is expected in the temperature interval $\Delta T=|T_c(H)-T| \ll H/|dH_{c_2}/dT|$. The scaling analysis on various high-T_c materials,[21] however, suggests that the actual scaling range is much wider.[22] Figures 3(a) and 3(b) show the magnetization data for fields $H \geq 10$ kOe scaled in the proper 3D (main panels) and 2D (insets) forms, respectively. The corresponding $T_c^{2D}(H)$ and $T_c^{3D}(H)$ parameters are listed in Table I. While for the $X=Cu(NCS)_2$ salt 2D scaling is of almost the same quality as 3D scaling, both scaling forms are found to be of somewhat lower quality for the $X=Cu[N(CN)_2]Br$ salt. We note, however, that the choice of T_c^{2D} and T_c^{3D} in both scaling forms is not unique. A collapsing of the

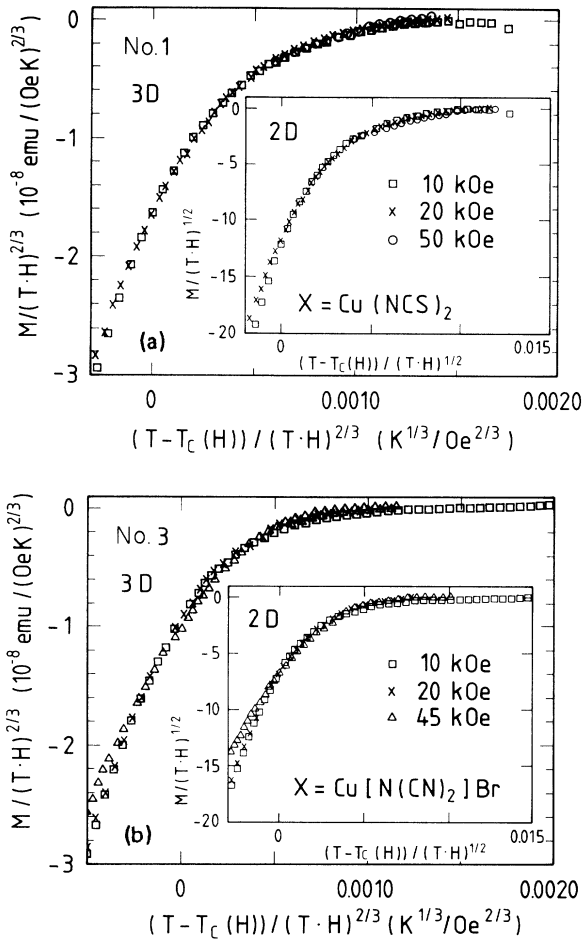

FIG. 3. 3D scaling of high-field magnetization curves for (a) $X=\mathrm{Cu(NCS)_2}$ and (b) $X=\mathrm{Cu[N(CN)_2]Br}$. Insets: 2D scaling behavior.

various $M(T,H)$ curves of similar quality is also achieved for slightly different sets of $T_c^{2D}(H)$ and $T_c^{3D}(H)$ values as, e.g., that given in the brackets for T_c^{3D}.

According to the above scaling behavior of *high-field* magnetization data for the $X=\mathrm{Cu(NCS)_2}$ salt, this material is located at the threshold from a highly anisotropic 3D to a 2D superconductor. Based upon a scaling form of magnetization data taken in *low* ($H<4$ kOe) and *moderate* ($H=10$ kOe) fields, Ito *et al.*[3] claimed a distinct 2D character for this salt.

TABLE I. Mean-field transition temperatures of κ-(BEDT-TTF)$_2X$ for $X=\mathrm{Cu(NCS)_2}$ and $\mathrm{Cu[N(CN)_2]Br}$ in various fields perpendicular to the planes ($H_\perp$) as determined by 2D scaling (T_c^{2D}), 3D scaling (T_c^{3D}), and linear extrapolations (T^{nucl}, see text).

X	$H_\perp$ (Oe)	T_c^{2D} (K)	T_c^{3D} (K)	T^{nucl} (K)
	20			9.14±0.05
$\mathrm{Cu(NCS)_2}$	10000	8.4	8.5 (8.35)	8.2±0.1
	20000	7.1	7.1 (6.9)	7.25±0.1
	50000	3.1	2.7 (2.5)	
	20			11.4±0.05
$\mathrm{Cu[N(CN)_2]Br}$	10000	11.1	11.25 (11.2)	11.1±0.05
	20000	10.35	10.45 (10.35)	10.79±0.15
	45000	8	8	9.6±0.2

Besides the scaling derived T_c^{2D} and T_c^{3D} values Table I contains also the nucleation temperatures T^{nucl} determined as follows: With decreasing temperature the range of maximum rounding in $M(T)$ is followed by a regime, where the magnetization is linear in T [cf. Figs. 1(a) and 1(b)]. We define the nucleation temperature as the intercept of the linear extrapolations from above and below the rounded $M(T)$ range.

C. Anisotropy in the upper critical field and coherence length

In order to determine the upper critical fields we plot the values for $T_c^{3D}(H)$ and $T^{nucl}(H)$ for the various fields in Figs. 4(a) and 4(b).[23] The horizontal bars indicate the range of possible $T_c^{3D}(H)$ values which lead to a scaling form of almost equal quality. Whereas the nucleation temperatures follow a linear dependence on H (except a shallow tail below 1 kOe, not shown) T_c^{3D} shows a peculiar field dependence, i.e., a weak reduction upon increasing the field from 0 to 10 kOe followed by a rapid decrease upon going to 20 kOe. Figures 4(a) and 4(b) also

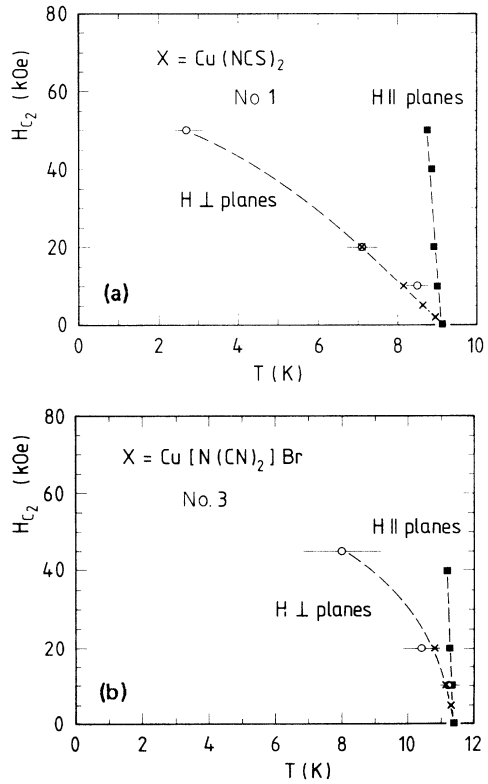

FIG. 4. Temperature dependence of the upper critical fields for fields perpendicular and parallel to the conducting planes including the 3D scaling derived T_c^{3D} (○) and the nucleation temperatures (×,■). The horizontal bars indicate the range of T_c^{3D} values which lead to a scaling form of almost identical quality. (a) for $X=\mathrm{Cu(NCS)_2}$ and (b) for $X=\mathrm{Cu[N(CN)_2]Br}$.

TABLE II. Initial slopes of the upper critical field and Ginzburg-Landau coherence length for fields $\perp$ and $\parallel$ to the conducting planes as well as the corresponding anisotropy ratio Γ of κ-(BEDT-TTF)$_2X$ for X=Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br.

X	$H_{c_2}^{\perp\prime}$ (kOe/K)	$H_{c_2}^{\parallel\prime}$ (kOe/K)	Γ	$\xi_\perp$ (Å)	$\xi_\parallel$ (Å)
Cu(NCS)$_2$	$-(13\pm3)$	$-(130\pm15)$	100	5.2±1	53±6
Cu[N(CN)$_2$]Br	$-(38\pm18)$	$-(210\pm30)$	30	4.9±1.5	28±5

include the nucleation temperatures for fields parallel to the conducting planes. Since for this configuration the transition is unaffected by fluctuation effects we consider $T^{\rm nucl}$ as the mean-field transition temperature.

For the initial slope of the upper critical field for this field configuration we find $H_{c_2}^{\parallel\prime}=dH_{c_2}^{\parallel}/dT=-(130\pm15)$ kOe/K and $-(210\pm30)$ kOe/K for the X=Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br salts, respectively. For fields perpendicular to the conducting planes an estimate of $H_{c_2}^{\perp\prime}$, is impeded by the uncertainty in the $T_c^{\rm 3D}$ values. As an average slope we use the linear field dependence of the nucleation temperatures of $-(13\pm3)$ kOe/K and $-(38\pm18)$ kOe/K for the X=Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br salts, respectively (the error margins reflect the uncertainties in $T_c^{\rm 3D}$).

Table II summarizes the results for H_{c_2}' for both field configurations as well as the corresponding values for the anisotropy ratio $\Gamma=(H_{c_2}^{\parallel\prime}/H_{c_2}^{\perp\prime})^2$. Since a small misalignment could strongly effect our estimate of $H_{c_2}^{\parallel}$, we consider the so derived Γ as a lower boundary. For the determination of the Ginzburg-Landau coherence length we use the relations $H_{c_2}^{\perp\prime}=\phi_0(2\pi)^{-1}\xi_\parallel^{-2}T_c^{-1}$ and $\xi_\perp/\xi_\parallel=H_{c_2}^{\perp\prime}/H_{c_2}^{\parallel\prime}$.[24]

For the X=Cu(NCS)$_2$ salt the above values for the Ginzburg-Landau coherence length slightly exceed those derived by Ito *et al.*[3] (by a factor of about 1.7) using a renormalized fluctuation theory.[25] However, these values differ significantly from those determined from the analysis of resistive transitions without taking fluctuation effects into account (for a list see Ref. 3 and references cited therein). The coherence length for the X=Cu[N(CN)$_2$]Br salt agrees within the experimental error with the values given by Ito *et al.*[3] and Kwok *et al.*[2]

D. Mixed-state properties: Irreversibility line

One of the peculiarities of the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br organic superconductors is the existence of an extended range in the H-T plane where the bulk magnetization is entirely reversible upon changing the field.[26] This phenomenon has been recognized first in the cuprate superconductors where it has attracted much interest from both technological as well as fundamental perspectives. The lower boundary of this region, which separates a magnetically irreversible, zero-resistive low-T state from a reversible high-T range with vanishing critical current J_c, is called the irreversibility line $H_{\rm irr}(T)$ or $T_{\rm irr}(H)$, respectively. Although numerous experiments have been devoted to study the exotic properties related to $H_{\rm irr}(T)$ in the cuprates, no consensus has been achieved so far as to its microscopic origin. Various explanations have been suggested including thermally assisted depinning,[27] the formation of a vortex glass,[28] or melting of the flux lattice.[29] Regardless of its underlying mechanism the following relations between $H_{\rm irr}(T)$ and material parameters have been found: (i) $H_{\rm irr}(T)$ far below $H_{c_2}(T)$ is a property of anisotropic superconductors with short coherence length; (ii) $H_{\rm irr}(T)$ is sensitive to the presence of defects of appropriate size, (iii) for different materials with com-

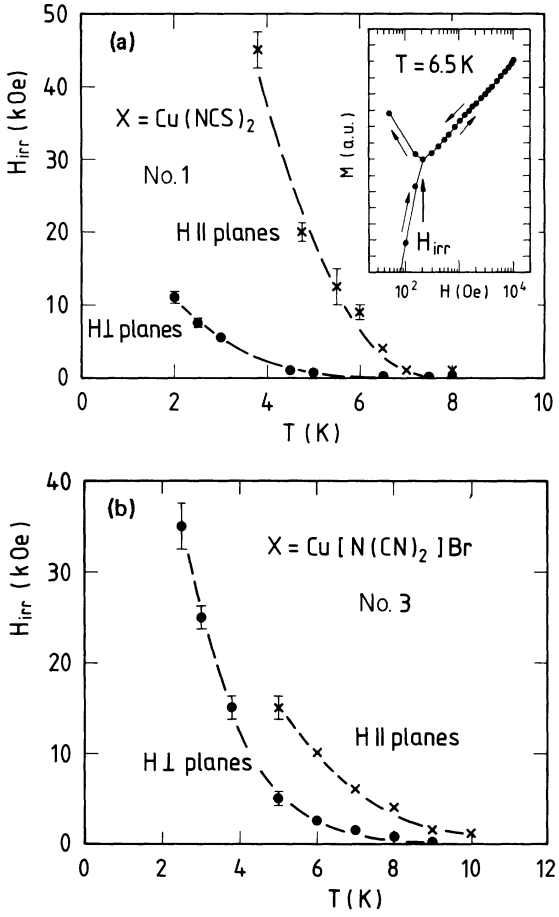

FIG. 5. Temperature dependence of the irreversibility line $H_{\rm irr}(T)$ for magnetic fields parallel and perpendicular to the conducting planes. (a) for X=Cu(NCS)$_2$ and (b) for X=Cu[N(CN)$_2$]Br. Inset of (a) shows the definition of $H_{\rm irr}$ as the field below which a magnetic hysteresis loop opens in an isothermal experiment.

parable defect structure the reversible range is wider for the more anisotropic systems.

Figures 5(a) and 5(b) show $H_{irr}(T)$ measured in fields perpendicular and parallel to the conducting planes for the $X=Cu(NCS)_2$ and $Cu[N(CN)_2]Br$ salts, respectively. Here, $H_{irr}(T)$ corresponds to the field value below which the magnetic hysteresis loop opens in a constant-temperature experiment [cf. inset of Fig. 5(a)]. Both salts show a most extended reversible range for fields perpendicular to the planes. In fact, the reversible regime is of comparable size to that of the $Bi_2Sr_2CaCu_2O_8$ compound in the same range of reduced temperatures $t=T/T_c$.[30] The reversible regime becomes smaller but remains finite also for fields parallel to the planes. For the $X=Cu(NCS)_2$ salt the anisotropy appears to be much more pronounced. We note, however, that small deviations from the exact $H\|$ plane alignment might have obscured the true anisotropy of $H_{irr}(T)$. We therefore refrain from a further analysis of $H_{irr}(T)$ for this field configuration. Figure 6 shows $H_{irr}(T)$ vs reduced temperature for fields perpendicular to the planes for both salts on a semilogarithmic plot. We find a similar T dependence of H_{irr} for both salts, where $H_{irr}(T)$ for the $X=Cu[N(CN)_2]Br$ salt is shifted to higher values by an almost constant factor of about 3.5 over the entire temperature range investigated. Within the experimental error the data shown in Fig. 6 are well described by an exponential T dependence, $H_{irr}(T)=H_0\exp(-AT/T_c)$, with $H_0=56$, 207 kOe and $A=7.3$, 8 for the $X=Cu(NCS)_2$ and $Cu[N(CN)_2]Br$ salts, respectively. The somewhat smaller reversible range for the $X=Cu[N(CN)_2]Br$ salt is consistent with a somewhat reduced anisotropy for this material compared to the $X=Cu(NCS)_2$ salt. An exponential dependence of $H_{irr}(T)$ for an intermediate temperature range has been reported also for various high-T_c cuprates (Ref. 31 and references cited therein). The actual width of the exponential range was found to vary between different systems and also to depend on the defect structure. For systems with moderate anisotropy it appears to be most extended and covers reduced temperatures of about $0.2\le t\le 0.8$. For the more anisotropic materials (as $Bi_2Sr_2CaCu_2O_8$), however, the exponential range shrinks and is described by a crossover behavior from a power law $H_{irr}(T)\sim(1-T/T_c)^{3/2}$ at low H and high T to an upturn in log $H_{irr}(T)$ at high fields and low temperatures. This upturn has been attributed to a peculiar vortex dynamics expected only for highly anisotropic materials.[31] The irreversibility line for the present materials does not show any signature of either an upturn at low temperatures nor a power-law behavior close to T_c. Future studies have to include measurements close to T_c ($t\ge 0.8$) and at low temperatures ($t\le 0.2$) as well as investigations of the dependence of $H_{irr}(T)$ on the defect structure in order to find a clue to the origin of the irreversibility line for the present materials in relation to the quasi-2D cuprates.

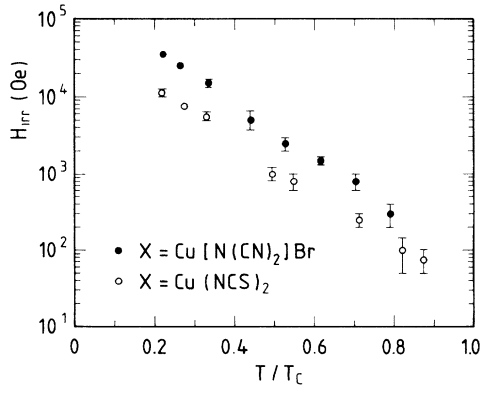

FIG. 6. Irreversibility line for H perpendicular to the planes vs reduced temperature T/T_c for both salts on a semilogarithmic scale.

E. Magnetic relaxation below the irreversibility line

In order to study further the nature of flux motion and its relation to the irreversibility line we have investigated the time dependence of the magnetization in a *field-cooled* experiment for the $X=Cu(NCS)_2$ salt. Magnetic-relaxation phenomena for this salt have been already studied by Mota *et al.*[32] after cooling the sample in *zero field* prior to the application of a short magnetic pulse. Figure 7 shows the magnetization after cooling the sample in a constant field of $H=100$ Oe from 15 K down to a temperature T'. After the sample had reached T', data were recorded every 100 sec. For $T'=8$ K $>T_{irr}(100$ Oe$)\approx 7$ K the bulk magnetization is independent of time within the resolution of our magnetometer. This observation is consistent with a highly mobile and pinning free vortex state above the irreversibility line. On the other hand, cooling down to temperatures $T'=4.5$, 5.5 K, i.e., $T'<T_{irr}(100$ Oe) is accompanied with a time-dependent increase of the diamagnetic magnetization with a $\ln t$ dependence for large t. The relaxation rate decreases upon going to lower temperatures. At $T'=4.5$ K the change in the magnetization within 1 h amounts to 10% during the first hour and remains still 2% after 30 h. From our field-cooled experiments across the irreversibility line we conclude that the vortex state below $H_{irr}(T)$ is

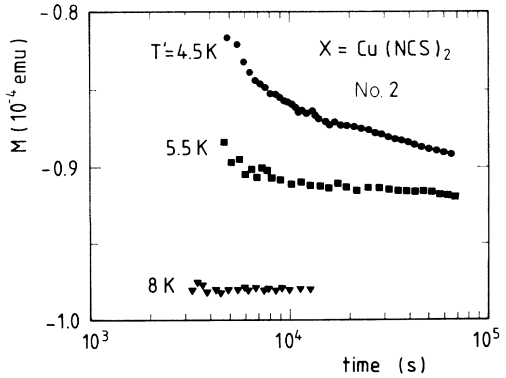

FIG. 7. Time dependence of the magnetization of the $X=Cu(NCS)_2$ salt after cooling in a constant field of $H=100$ Oe applied perpendicular to the planes down to T'. The temperatures $T'=4.5$ and 5.5 K are below the irreversibility line for this field.

metastable, which implies that the magnetization depends on the previous path in the H-T plane. It is clear that experiments performed within the irreversible range are unavoidably affected by these relaxation processes; a fact which might be of crucial importance for the interpretation of low-T experiments in the mixed state as, e.g., low-T muon-spin-rotation experiments intended to examine the T dependence of the London penetration depth.[33,34] In the light of this we believe that the deviations between the results reported by Le *et al.*[33] and Harshman *et al.*[34] which happen to occur just upon entering the irreversible range are related to this problem.

F. Consequences of the vortex dynamics on the determination of the London penetration depth from the reversible magnetization

From the magnetization data taken as a function of both field and time we conclude that on a macroscopic scale the reversible range can be characterized as a homogeneous and thermodynamically stable state. As has been pointed out by Clem[35] the microscopic view of a vortex in a strongly anisotropic material is no longer a continuous flux line. Instead, the confinement of the screening currents to the superconducting layers causes a segmentation of the vortices into 2D vortex pancakes. Bulaevskii, Ledvij, and Kogan have shown that for fields perpendicular to the planes thermal distortions of vortex segments out of the straight stacks result in an extra contribution to the entropy and thus to the free energy of the system.[14] This also has consequences for the magnetization M measured as a function of field at constant temperature. These authors found that the presence of such fluctuations does not alter the linear $M(\ln H)$ dependence as predicted by the London model and observed in high-T_c as well as in the present organic superconductors.[4,5] The effect of fluctuations manifests itself in a T-dependent correction factor $g(T)$, where $g(T)=0$ in the simple London model. According to their model, the slope of the magnetization is given by

$$\frac{\partial M}{\partial \ln H}=\frac{\phi_0}{32\pi^2\lambda_\parallel^2}\times[1-g(T)]\ , \tag{1}$$

where $g(T)=32\pi^2 k_B/(\phi_0^2 s)T\lambda_\parallel^2(T)$, s is the effective interlayer distance, and $\lambda_\parallel$ is the in-plane London penetration depth. The London model [$g(T)=0$] has been used in Refs. 4 and 5 to determine the temperature dependence of λ from the linear $M(\ln H)$ behavior in the reversible range. In order to estimate the contribution of thermal fluctuations to $M(H)$ and $\lambda(T)$ shown in Refs. 4 and 5, one has to compare $g(T)$ with unity. This, however, requires a knowledge of the effective interlayer distance s. To give a consistent estimate of $g(T)$ within the model of Bulaevskii *et al.*, we use $s=(k_B T^*)/(-\phi_0 M^*)$, a relation which follows from the above model for the universal point $M^*(T^*,H)$ (cf. Sec. III A). The so-derived correction factor becomes substantial only close to T_c. At low temperatures, however, the correction is of the order of a few percent. At $T=6$ K, for example, it amounts 2.5% and for $T\leq 3$ K it is less than 1%. According to the above reasoning, which is based on a 2D situation, vortex fluctuations have only little effect on the slope of the linear $M(\ln H)$ range for the present materials. Hence, vortex fluctuations do not affect the main conclusion drawn from measurements of the reversible magnetization,[4,5] namely, that the London penetration depth $\lambda(T)$, for the present superconductors has an exponentially small T dependence at lower temperatures consistent with a conventional order parameter.

IV. CONCLUSION

We have presented high-resolution dc-magnetization data near the superconducting transition and in the mixed state of the organic superconductors κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. For fields perpendicular to the conducting planes both systems show clear signatures of strong superconducting fluctuations, i.e., a pronounced rounding of $M(T,H)$ near T_c accompanied by a field-dependent slope below, and a field-induced diamagnetic contribution at temperatures as high as $2\times T_c$. A closer inspection of the magnetic behavior revealed a crossing point for the various $M(T,H)$ curves close to T_c for small and moderate fields and a scaling form for the high-field data. While for the $X=$Cu(NCS)$_2$ salt 2D scaling works almost equally well as 3D scaling, both scaling forms are of lower quality for the $X=$Cu[N(CN)$_2$]Br salt. Within the uncertainties of the corresponding $T_c^{2D}(H)$ and $T_c^{3D}(H)$ values the nucleation temperature $T^{nucl}(H)$ provides a satisfactory average, which allowed for a determination of the upper critical-field slopes and their anisotropies. Using a BCS extrapolation formula we find a Ginzburg-Landau coherence length of $\xi_\perp=(5.2\pm1)$ Å, $\xi_\parallel=(53\pm6)$ Å ($\Gamma\geq 100$) for $X=$Cu(NCS)$_2$ and $\xi_\perp=(4.9\pm1.5)$ Å, $\xi_\parallel=(28\pm5)$ Å ($\Gamma\geq 30$) for $X=$Cu[N(CN)$_2$]Br, respectively. Due to the possibility of small misalignments we consider the anisotropy ratios given in the parentheses as a lower boundary. A characteristic of the mixed state is the existence of an irreversibility line, $H_{irr}(T)$, far below $H_{c_2}(T)$. The reversible range is more extended for H perpendicular to the planes but remains finite also for H parallel to the planes. For both salts we find an exponential temperature dependence of H_{irr} for fields perpendicular to the planes. Relaxation phenomena observed after cooling the sample in a constant field across the irreversibility line demonstrated that the vortex state below H_{irr} is metastable. Consequences of the anomalous vortex state below (metastability) and above (vortex fluctuations) $H_{irr}(T)$ on mixed-state derived properties, such as the London penetration depth, have been pointed out. In particular, according to the model proposed by Bulaevskii, Ledvij, and Kogan[14] vortex fluctuations do not affect the conclusions drawn from measurements of the reversible magnetization,[4,5] namely, that the London penetration depth for the present materials has an exponentially small T dependence at low temperatures consistent with a conventional order parameter.

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