Critical fields and mixed-state properties of the layered organic superconductor κ-(BEDT-TTF)$_2$I$_3$

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(Received 8 September 1995)

We report on a systematic study of the thermodynamic superconducting properties on high-quality crystals of the quasi-two-dimensional (quasi-2D) organic superconductor κ-(BEDT-TTF)$_2$I$_3$. Low-field magnetization measurements served to determine the lower critical field B_{c1}. Just below T_c=3.5 K, down to ~ 3 K, B_{c1} perpendicular ($\perp$) to the highly conducting BEDT-TTF layers is found to be strongly suppressed below the sensitivity limit of the instrumental resolution. This might be an indication for single-vortex fluctuations expected for a strongly 2D superconductor. The critical field B^*_{c2} determined by ac-susceptibility measurements is found to be related to an irreversibility line. The temperature and frequency dependences of B^*_{c2} are consistent with well-established flux-creep models. The upper critical field $B_{c2\perp}$ extracted from magnetization measurements is consistent with specific-heat data. For both principal field orientations a crossover of the critical-field slopes $|dB_{c2}/dT|$ towards a shallow tail close to T_c is observed. Apparent discrepancies of the thermodynamic critical fields for parallel and perpendicular field orientation are found, indicating either a strongly reduced $B_{c1\parallel}$ or $B_{c2\parallel}$.

I. INTRODUCTION

Since the first observation of superconductivity in a metal based on organic molecules, the number of superconducting organic materials has been continously growing.[1] The largest number of organic superconductors has a quasi-two-dimensional (quasi-2D) electronic structure. From measurements of magnetic quantum oscillations the Fermi surface of many organic metals is well known and shows the textbook-like 2D topology.[2] Due to this reduced dimensionality, distinctive new physical properties are expected and have indeed been found. A large number of experimental data on the superconducting properties of organic metals already exists. Up to date, however, the nature of the superconducting state is still far from being understood. The possibilities of the usual BCS-type or a more exotic origin are under considerable debate. This unclear and unsatisfactory situation is partly caused by ambigous and sometimes contradictory experimental results.

The organic metals are extreme type-II superconductors with coherence lengths perpendicular to the conducting planes, $\xi_\perp$, of less than the interlayer spacing. Therefore, enhanced fluctuation effects are expected and have been observed experimentally.[3] In addition, the mixed state in the superconducting phase diagram is very large and the pinning forces in the very pure materials are expected to be small. Therefore, flux-flow and irreversibility effects should play an important role in the superconducting state. Consequently, ignoring these effects might be the reason for the experimental inconsistencies. Especially, superconducting parameters extracted from transport measurements in magnetic field are highly ambiguous. Thereby, as we will show later, a magnetic field as small as the earth's field has already an appreciable influence on the superconducting phase transition. Consequently values of critical fields, coherence lengths, and other superconducting parameters derived from resistivity or ac-susceptibility data are only approximate and might have little to do with true thermodynamic quantities. Therefore, thorough investigations are needed to gain more information on the nature of the superconducting state in these synthetic metals. In addition, since the discovery of quasi-2D high-T_c cuprates clarifying studies to obtain a better understanding of the principal superconducting behavior of layered materials have become a major point of interest from both the experimental and theoretical sides. The 2D organic metals can serve here as model systems for the study of layered superconductors due to their almost perfect two dimensionality and since the whole superconducting field-temperature parameter space can be reached with standard experimental equipment. Meanwhile very pure single crystals of appreciable sizes (a few mg) are available which allow systematic investigations of bulk properties.

Salts of the type (BEDT-TTF)$_2X$, where BEDT-TTF stands for bisethylenedithio-tetrathiafulvalene and X represents a monovalent anion, comprise the largest number of organic superconductors. The 2D materials with the to-date highest superconducting transition T_c approaching 13 K are all members of the κ phase of (BEDT-TTF)$_2X$.[4] Here we present dc-magnetization and ac-susceptibilty measurements of another κ-phase salt, namely, κ-(BEDT-TTF)$_2$I$_3$, with T_c=3.5 K.[5,6] From the data the lower and upper critical fields for fields parallel and perpendicular to the highly conducting BEDT-TTF layers have been determined. A possible small anisotropy of the coherence length $\xi_{\parallel}$ within the BEDT-TTF planes has not been determined and will be neglected in the following. A comparison with specific-heat data[7] is made and a complete set of the superconducting parameters of κ-(BEDT-TTF)$_2$I$_3$ is given. The observed irreversibility and fluctuation effects will be discussed in detail.

II. EXPERIMENTAL DETAILS

The investigated platelike single crystals were prepared by the standard electrochemical process described in detail elsewhere.[8] The crystal structure is monoclinic with space group $P2_1/c$. The BEDT-TTF molecules form layers in the b-c plane which are separated by layers of I_3^- anions alternately stacked along the a direction. Most measurements we report on were made on pieces of the same crystal where previously the specific heat[7] and the de Haas–van Alphen (dHvA) effect[9] have been studied. The latter measurement and the observed Meissner fraction of more than 70% revealed the high quality of the sample. Comparison with the specific-heat data allows a direct thermodynamic consistency check of the extracted superconducting parameters.

The ac susceptibility was measured down to 0.45 K in a toploading ^{3}He cryostat equipped with a superconducting magnet for fields up to 13 T. The induced complex ac signal was detected in a compensated pickup coil system with the usual lock-in technique. For most measurements the modulation field amplitude was kept below 0.2 mT at a modulation frequency of $\sim$ 78 Hz. Checks with different amplitudes during field sweeps revealed a neglegible shift of the diamagnetic onset (which we defined as the critical field B_{c2}^*), but also, however, an appreciable broadening of the transition width. The susceptibility data were taken by magnetic-field sweeps at constant temperature. The sample could be rotated *in situ* around one axis with a relative accuracy of better than 0.1°. The absolute value of the orientation angle was calibrated either by the 1/cosΘ dependence of the dHvA frequency[2,9] or by the maximum critical field reached for B parallel to the BEDT-TTF planes (cf. Fig. 6).

The magnetization M was measured in a home-built superconducting quantum interference device (SQUID) magnetometer. The lowest temperature we could reach was $\sim$ 2 K. The whole cryostat was shielded by μ metal against external fields which reduced the magnetic field at the place of the sample to $\sim$ 1 μT. The residual field could further be reduced by applying a small counterfield. The magnetization data were taken at constant fields as a function of temperature. The absolute value of M was calibrated against a Pb sphere. The investigated samples revealed complete shielding within experimental resolution ($\pm 5\%$). The demagnetization factors of the samples were estimated from their geometrical shape and found to be in agreement with the observed initial slopes of the magnetization curves (see Fig. 2).

III. RESULTS AND DISCUSSION

A. Lower critical fields

Figure 1 shows the low-field magnetization of κ-(BEDT-TTF)$_2$I$_3$ in different fields between 0.4 μT and 5 mT applied perpendicular to the conducting BEDT-TFF planes. The data are taken in the shielding modus; i.e., the sample is first cooled down, then the magnetic field is applied in the superconducting state, and finally the temperature is raised slowly up to temperatures above T_c. Already for the lowest field a relatively broad superconducting transition ($\Delta T \approx 0.3$ K) compared to the conventional superconductors is found. Below $\sim$ 3 K the full diamagnetic signal is observed. With increasing field the diamagnetic onset shifts only slightly for the shown field range. The transition width, however, increases considerably. Already for an applied field $B_a = 1$ mT the full diamagnetic signal is no longer reached (presumably not even for $T \rightarrow 0$). Note also that for B_a of the order of the Earth's field ($\sim$ 0.05 mT) the transition has broadened to $\Delta T \approx 0.5$ K. This behavior seems to be partially due to fluctuation effects. An estimate of the relevant temperature region where fluctuations should play a dominant role can be obtained by the Ginzburg criterion[10]

$$|\Delta t| \equiv \left| \frac{T - T_c}{T_c} \right| \leqslant \frac{1}{32\pi^2} \left(\frac{\mu_0 k_B T_c}{B_{c\mathrm{th}}} \frac{1}{\xi_{\parallel}^2 \xi_{\perp}} \right)^2, \qquad (1)$$

where k_B is the Boltzmann factor, μ_0 is the permeability of vacuum, and $B_{c\mathrm{th}}$ is the thermodynamic critical field. With $B_{c\mathrm{th}} = 0.02$ T and the coherence lengths as given below a value of $\Delta t \approx 2 \times 10^{-5}$ is extracted. With a different estimate taking higher-order fluctuation corrections into account[11] an even larger value of $\Delta t \approx 3 \times 10^{-4}$ is obtained. Although these temperature regions are considerably larger than values for conventional superconductors, they can by far not explain the observed broadening of the transitions. As will be discussed in more detail later the initial diamagnetic signal broadens appreciably already in very small fields, indicating the importance of measurements in as small fields as possible.

Other reasons for the temperature dependence of the diamagnetic response of the samples are demagnetization effects and extremely small values of the lower critical field B_{c1}. Since the samples were thin plates, the demagnetization factor for B perpendicular to the BEDT-TTF planes was found to be of the order $N \approx 0.75$. This means that the field acting on the samples decreases during the temperature sweeps from $B_a/(1-N)$ at the lower critical field down to B_a (= the applied magnetic field) at the upper critical field.

B_{c1} was extracted from the magnetization data in the usual way done for type-II superconductors.[12] First, the field dependence of M for fixed temperatures was read out of data like those shown in Fig. 1 for the different applied fields B_a. The resulting field-dependent magnetization for selected temperatures is shown in Fig. 2 for B perpendicular and parallel to the planes. M exhibits the typical well-known behavior for type-II superconductors. Up to B_{c1} the magnetization follows the ideally diamagnetic behavior represented by the solid lines in Fig. 2. Above this temperature-dependent field the data points gradually fall below this line. B_{c1} defined by this first deviation from linearity is an upper limit which might be enhanced due to possible flux pinning. The exact behavior of $M(B)$ in the mixed state above B_{c1} and below B_{c2} depends strongly on the sample shape and demagnetization effects. Numerical simulation approximating the sample

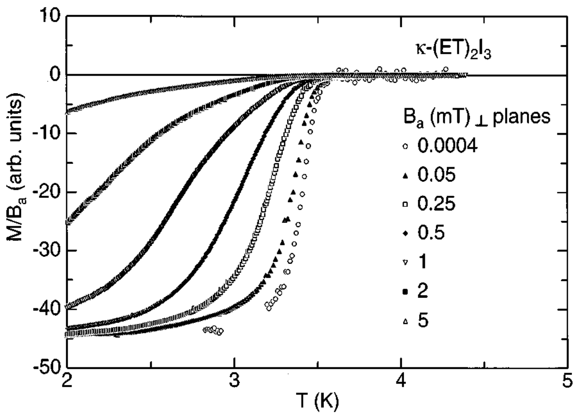

FIG. 1. Temperature dependence of the magnetization of κ-(BEDT-TTF)$_2$I$_3$ for different fields applied perpendicular to the BEDT-TTF planes. The data are normalized by the applied external field.

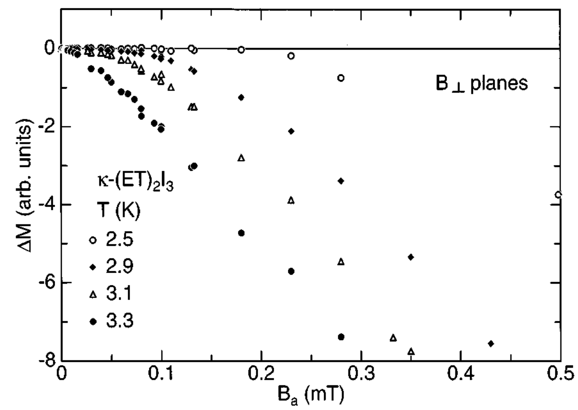

FIG. 3. Field dependence of the magnetization difference between ideally diamagnetic response and measured values for different temperatures.

shape by an ellipsoid could describe the $M(B)$ curves for high-T_c materials[13] and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (Ref. 14) reasonably.

A reliable way to determine the field where the first deviation from linearity occurs is a plot of the field-dependent magnetization difference between the ideal diamagnetic value $M_{\rm dia}$ shown as the solid line in Fig. 2 and the measured value M. This difference $\Delta M = M_{\rm dia} - M$ is shown in Fig. 3 for the same data as plotted in Fig. 2(a). B_{c1} is easily extractable from the points where ΔM deviates from zero, e.g., for $T = 2.5$ K at $B_a \approx 0.2$ mT. From the data shown in Fig. 3 it is already obvious that $B_{c1\perp}$ becomes extremely small at higher temperatures since ΔM deviates from zero already for the lowest applied fields.

The temperature dependence of B_{c1} corrected by the demagnetization factor ($N = 0$ for B parallel to the planes) is shown in Fig. 4 for both principal directions. For B perpendicular to the BEDT-TTF planes an unexpected behavior is

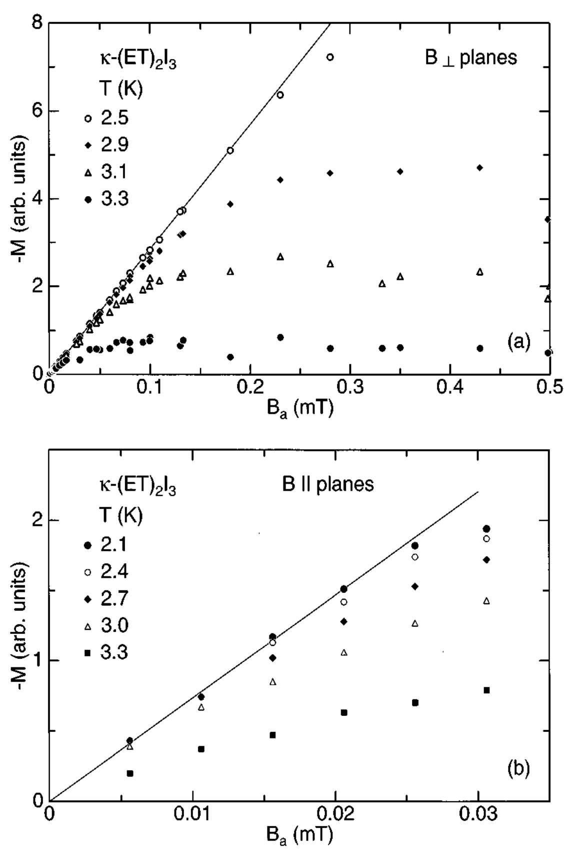

FIG. 2. Field dependence of the magnetization at different temperatures for B (a) perpendicular and (b) parallel to the BEDT-TTF planes. The data are extracted from curves as shown in Fig. 1. The solid line shows the ideal diamagnetic behavior.

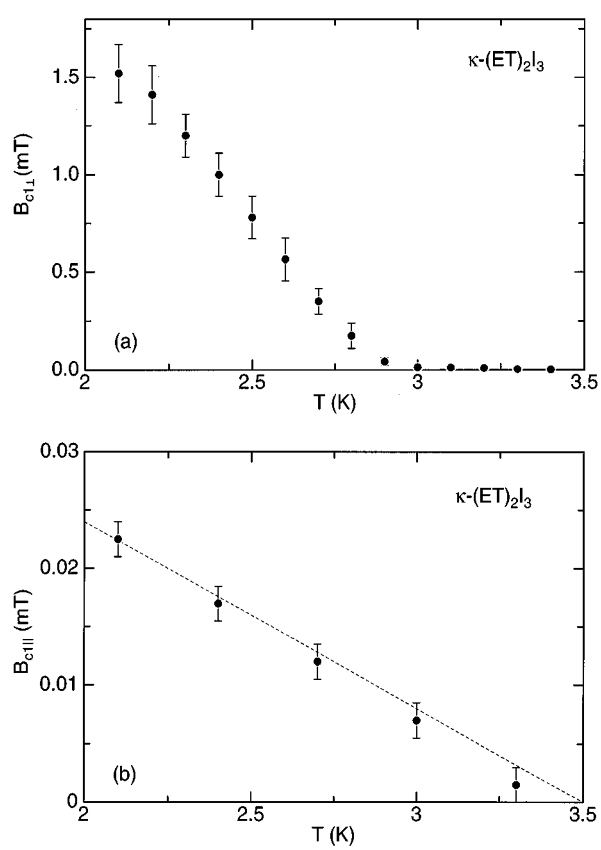

FIG. 4. Lower critical field B_{c1} for B (a) perpendicular and (b) parallel to the BEDT-TTF planes. For (a) the demagnetization factor has been taken into account.

found. From $T_c=3.5$ K down to ~ 3 K, B_{c1} is below the sensitivity limit of our apparatus. Towards lower temperatures B_{c1} increases approximately linearly and seems to level off at the lowest temperature measured. A rough linear extrapolation of $B_{c1\perp}$ towards $T=0$ results in (4 ± 1) mT. For B parallel to the BEDT-TTF planes no such strong reduction of $B_{c1\parallel}$ close to T_c is observed. Within experimental resolution the extracted $B_{c1\parallel}$ values are compatible with the dashed linear line [see Fig. 4(b)]. However, due to the extreme smallness of $B_{c1\parallel}$, the data points have relatively large error bars. Especially $B_{c1\parallel}$ at 3.3 K might be zero already. The extrapolated lower critical field is $B_{c1\parallel}(0)\approx 0.05$ mT which is a factor 80 smaller than $B_{c1\perp}$ showing the extreme two dimensionality of the superconducting properties in κ-(BEDT-TTF)$_2$I$_3$.

Analogous determinations of $B_{c1\perp}(T)$ for the isostructural salt κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ have revealed a tendency for an upward curvature of $B_{c1\perp}$ towards lower temperatures.[15] However, these authors found no suppression of $B_{c1\perp}$ close to T_c within experimental resolution. In a later work on the same material another group reported a linear decrease of $B_{c1\perp}(T)$.[14] Thereby, however, the critical-field line extrapolates to zero at $T\approx 7.5$ K whereas T_c of the sample was ~ 9 K (onset of a diamagnetic signal). Indeed, our own preliminary measurements on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ verify the results of Ref. 14 and show a similar reduction of $B_{c1\perp}$ close to T_c as found here for κ-(BEDT-TTF)$_2$I$_3$ [see Fig. 4(a)].

A suppression of the lower critical field $B_{c1\perp}$ comparable to the one described above was observed for the cuprate superconductor $Bi_2Sr_2CaCu_2O_8$, a system revealing highly 2D behavior, too.[16] A theoretical explanation of the reduced lower critical field has been given by Blatter *et al.*[17] They considered fluctuations of individual vortices in strongly 2D material. The main result was an observable downward renormalization of $B_{c1\perp}$ close to T_c over a range given by

$$\Delta\tau\approx\frac{k_BT_0}{\epsilon_0(0)d}\ln\frac{\tau_R}{\tau_G}, \tag{2}$$

where T_0 is the bare transition temperature without fluctuations, d is the interlayer distance, and $\epsilon_0=(\Phi_0/\lambda_\perp)^2(1/4\pi\mu_0)$ determines the relevant energy scales for vortex fluctuations. Φ_0 is the flux quantum, and $\lambda_\perp$ is the London penetration depth for planar currents. $\tau_G\equiv 1-T_G/T_0=k_BT_0/\epsilon_0(0)d$ is the extent of the critical fluctuations, i.e., the Ginzburg region up to the temperature T_G for a 2D superconductor. The reduced temperature τ_R given by the implicit equation $\tau_R=\tau_G\ln(1/\tau_R)$ describes the relative reduction of B_{c1} due to fluctuations within the Gaussian approximation. For $Bi_2Sr_2CaCu_2O_8$ a relative reduction of $\Delta\tau\approx 0.03$ was estimated[17] which is in good accordance with the observed value.[16] Using the parameters for κ-(BEDT-TTF)$_2$I$_3$ derived later in detail (see Table I) we obtain $\Delta\tau\approx 0.013$. This value is by far too small to account for the observed effect. In the derivation of τ_{c0} we used the lattice parameter $a\equiv d=1.64$ nm as the superconducting layer thickness which might be an overestimation. Nevertheless, for κ-(BEDT-TTF)$_2$I$_3$ the qualitative behavior of B_{c1} is similar as in the 2D cuprate superconductor. Quantitatively, however, the effect in the organic compound is much larger than expected theoretically. Preliminary results for the organic superconductors κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ ($T_c\approx 9$ K) and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br ($T_c\approx 11$ K) show similar absolute values (~ 0.5 K) for the downward curvature of $B_{c1\perp}$.[18] This suggests an intrinsic origin common in the 2D organic materials which most probably is caused by fluctuations due to the layered structure.

B. Mixed-state properties

Organic superconductors are known to have a large Ginzburg-Landau (GL) parameter $\kappa=\lambda/\xi$ with, therefore, a large mixed-state region in the B-T phase diagram. The behavior of the flux-line lattice and vortex dynamics in the mixed state are under intense study, pushed mainly by numerous investigations on high-T_c cuprates during the last five years.[19] Up to date, however, we are far from a general understanding of either the equilibrium phase or the dynamics of vortices. For organic superconductors these different pinning effects of the vortices are present as well and will therefore influence transport and magnetic measurements. In early studies of these layered and strongly type-II superconductors these effects often have not been taken into account properly in the data analysis.

Figure 5 shows the field dependence of the real part of the ac susceptibility χ for different field orientations at $T\approx 0.6$ K. Thereby, the angle $\Theta=0°$ represents an orientation of the field normal to the BEDT-TTF layers (both ac field and the steady field of the superconducting solenoid are parallel). The modulation-field frequency was approximately 78 Hz. The data for different angles are normalized, resulting in a seemingly larger scatter of the data at larger angles where the signal change is smaller and the sensitivity of the experimental setup is reduced (the pickup coils are rotated together with the sample). In the superconducting state χ is smoothly increasing up to a certain field where an almost steplike behavior of χ is observed. The onset of these steps is

TABLE I. Anisotropic superconducting parameters of κ-(BEDT-TTF)$_2$I$_3$ derived from critical-field data for B perpendicular ($\perp$) and parallel ($\parallel$) to the conducting layers. B_{c1}, B_{c2}, and B_{cth} are the lower, upper, and thermodynamic critical fields, respectively. κ is the Ginzburg-Landau parameter, ξ is the coherence length perpendicular ($\xi_\perp$) and parallel ($\xi_\parallel$) to the field, and λ is the London penetration depth for field perpendicular ($\lambda_\perp$) and parallel ($\lambda_\parallel$) to the planes.

	$B_\perp$		$B_\parallel$
T_c (K)		3.5	
B_{c1} (mT)	4		0.05
B_{c2} (T)	0.2		7
B_{cth} (mT)	20		7
B_{cth} [a] (mT)		17	
κ	7		675
$\xi_\perp$ (nm)		1.1	
$\xi_\parallel$ (nm)		41	
$\lambda_\perp$ (nm)		300	
$\lambda_\parallel$ (μm)		70	

[a]Derived from specific-heat data.

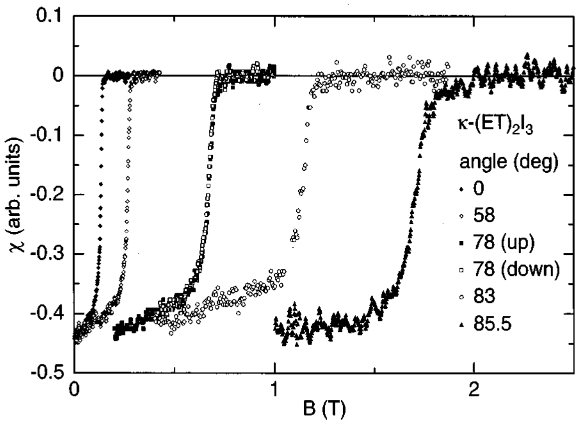

FIG. 5. Field dependence of the ac susceptibility of κ-(BEDT-TTF)$_2$I$_3$ for different angles at $T \approx 0.6$ K. The frequency of the modulation field was 78 Hz. For 78° data for an upward and downward field sweep are shown. No hysteresis is observed.

defined as B_{c2}^*. Above this value χ is field independent. No hysteresis in χ is observed as can be seen in Fig. 5 for the data at $\Theta = 78°$ which are plotted both for increasing and decreasing field.

The angular dependence of B_{c2}^* for two different temperatures is plotted in Fig. 6. The strong anisotropy can be seen clearly. Close to $\Theta = 90°$, B_{c2}^* increases sharply. For higher temperatures (the data at $T = 2$ K are shown as an example) close to $\Theta = 90°$ no reliable determination of B_{c2}^* was possible due to a decreasing signal-to-noise ratio. The solid curves are fits using the implicit relation for the critical field of 2D superconducting thin films given by Tinkham,[20]

$$1 = \left| \frac{B_{c2}^*(\Theta)\cos\Theta}{B_{c2\perp}} \right| + \left(\frac{B_{c2}^*(\Theta)\sin\Theta}{B_{c2\parallel}} \right)^2 . \tag{3}$$

A perfect description of the data at $T = 0.55$ K is obtained with $B_{c2\perp} = 0.15$ T and $B_{c2\parallel} = 6.7$ T. The angular dependence of B_{c2}^* (often equalized to the upper critical field B_{c2}) has been measured by different groups for different organic superconductors.[21] So far, however, it was not possible to distinguish decisively whether the Tinkham formula (3) or the 3D anisotropic Ginzburg-Landau formula

$$1 = \left(\frac{B_{c2}^*(\Theta)\cos\Theta}{B_{c2\perp}} \right)^2 + \left(\frac{B_{c2}^*(\Theta)\sin\Theta}{B_{c2\parallel}} \right)^2 \tag{4}$$

is more appropiate. The inset of Fig. 6 shows the data for $T = 0.55$ K close to $\Theta = 90°$ in an expanded scale. Again the solid line is the Tinkham fit according to (3), and the dashed line is the best fit using (4). Both $B_{c2\perp}$ and $B_{c2\parallel}$ are fit parameters. Clearly the Tinkham formula gives the better description of the data, especially close to the peak at $\Theta = 90°$. This again proves the strong two dimensionality of κ-(BEDT-TTF)$_2$I$_3$. At higher temperatures close to T_c due to the increasing coherence length $\xi_\perp$ a crossover to the GL formula (4) should occur. However, as mentioned above, the decreasing experimental resolution hampered a decisive verification of this conjecture.

Another point which has to be discussed carefully is how far the field B_{c2}^* extracted from the ac-susceptibility data is related to the thermodynamically relevant quantity, the upper critical field B_{c2}, for which (3) and (4) were derived originally. From earlier work on high-T_c cuprates it is known that B_{c2}^* is related to the so-called irreversibility line which shows a distinctive temperature and frequency dependence.[22] In the following we will show that indeed for organic superconductors B_{c2}^* shows the characteristic features of an irreversibility line as well.

First we consider the frequency dependence: Figure 7 shows B_{c2}^* over three decades of modulation-field frequency for two different field orientations at $T = 0.55$ K. The dashed lines represent fits of the form $B_{c2}^* \propto \ln(f_0/f)^{-2/3}$. This dependence is expected for thermally activated flux creep[22,23] as will be discussed later in more detail. For the characteristic attempt frequency f_0 best values of $f_0 \simeq 10^{17}$ Hz and $f_0 \simeq 10^{19}$ Hz were found for the data at $\Theta = 0°$ and $\Theta = 83°$, respectively. These are extraordinary large values.[22] However, within experimental accuracy for the data at $\Theta = 0°$ values between 10^{14} Hz and 10^{20} Hz are possible as well. For both angles the relative increase of B_{c2}^* is almost the same, namely, $\sim$ 13% for the measured frequency range. For temperatures closer to T_c the relative changes of B_{c2}^* with frequency become larger and the fitted values of f_0 decrease continuously towards $f_0 \approx 5 \times 10^6$ Hz at $T = 3.29$ K (data not shown).

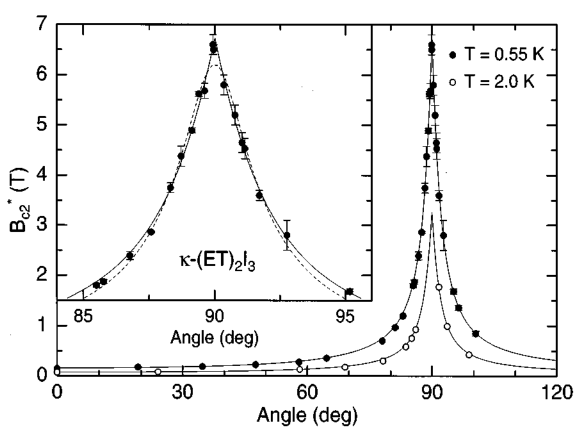

FIG. 6. Angular dependence of the critical field B_{c2}^* obtained from ac-susceptibility measurements for two different temperatures. The inset shows the region close to B parallel to the planes (90°) in an expanded scale. The solid lines are fits according to the 2D model of Tinkham (3), and the dashed line is a fit using the anisotropic effective mass model (4).

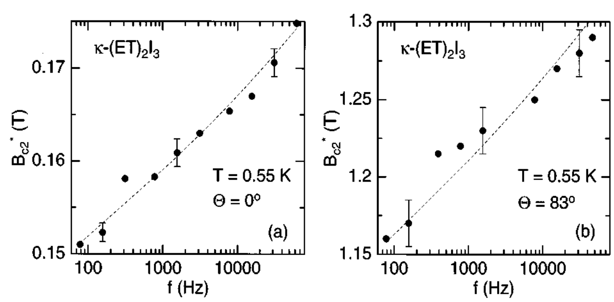

FIG. 7. Frequency dependence of the critical field extracted from ac susceptibility at $T = 0.55$ K for (a) $\Theta = 0°$ and (b) $\Theta = 83°$. The dashed lines represent fits of the form $B_{c2}^* \propto \ln(f_0/f)^{-2/3}$ as described in the text.

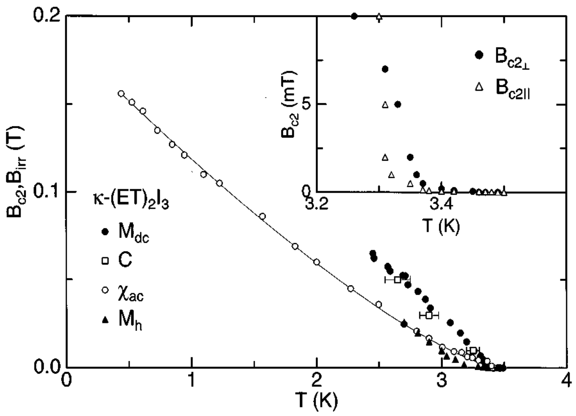

FIG. 8. Temperature dependence of the critical fields obtained from ac-susceptibility, specific-heat, and magnetization data as shown in Figs. 9 and 10. The solid line is a fit of the ac-susceptibility data according to (6). The inset shows the temperature dependence of B_{c2} obtained from magnetization data close to T_c in an enlarged scale.

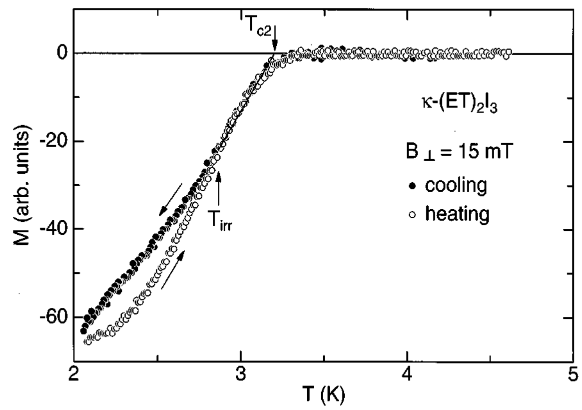

FIG. 9. Temperature dependence of the Meissner signal of κ-(BEDT-TTF)$_2$I$_3$ for a field of 15 mT applied perpendicular to the BEDT-TTF planes. Solid symbols show the data taken during cooling, and the open symbols represent data taken during heating. The temperature where both curves merge is defined as the irreversibility point, T_{irr}. The linear extrapolation of the magnetization in the superconducting state to $M=0$ gives the critical temperature T_{c2} for the applied field.

This result indicates clearly that for organic superconductors (like for the high-T_c cuprates) B_{c2}^* determined by ac susceptibility is different from the thermodynamic B_{c2} but labels rather the field where flux lines get pinned and are no longer able to follow the applied ac field within the time scale set by the characteristic measuring frequency. Whether B_{c2} follows the same angular dependence as B_{c2}^* is still an open question and remains to be checked. However, our results for B_{c2}^* suggest a similar behavior also for the thermodynamic quantity.

The next point we discuss is the temperature dependence of B_{c2}^*. Figure 8 shows the temperature dependence of the critical field determined by ac-susceptibility (open circles). The data reveal the typical positive curvature of this critical-field line observed previously for many other organic superconductors by ac susceptibility and resistivity measurements. The basic idea of the semiquantitative theory mentioned[22,23] is that pinned vortices can be activated thermally over an energy barrier U_0 which leads to a reduced critical current of the form[22]

$$J_c=J_{c0}[1-(k_BT/U_0)\ln(f_0/f)], \tag{5}$$

where J_{c0} is the critical current in the absence of thermal activation. $J_c=0$ defines the irreversibility point at the temperature T_{irr} and the field B_{c2}^*. U_0 scales as the condensation energy for a characteristic volume $B_{c\mathrm{th}}^2 V/2\mu_0$. Usually the thermodynamic critical field $B_{c\,\mathrm{th}}$ near T_c scales like $B_{c\mathrm{th}} \propto(1-t)$, with $t=T/T_c$. Different models exist to estimate the characteristic excitation volume V.[22] In our case the best description of the data is obtained by the assumption that $V \propto a_0^3$, where $a_0=1.075\sqrt{\Phi_0/B}$ is the flux-line spacing in a field B. Therefore, $U_0\propto(1-t)^2/B^{3/2}$. Approximating T by T_c and solving (5) for $J_c=0$ results in

$$B_{c2}^*\propto(1-t)^{4/3}[\ln(f_0/f)]^{-2/3}. \tag{6}$$

From this equation the frequency dependence of B_{c2}^* already mentioned can be recognized. The solid line in Fig. 8 is the one-parameter fit using above equation for fixed f. The data can be described perfectly by (6) down to the lowest temperature of ~ 0.45 K. The exact temperature dependence of B_{c2}^* depends on the detailed nature of the pinning centers and may vary between different materials and even between different quality samples. Indeed, for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br an exponential dependence $B_{c2}^*\propto\exp(-AT/T_c)$, with a fitting parameter A, was found.[3]

To further elucidate the irreversibility effects in κ-(BEDT-TTF)$_2$I$_3$ we performed Meissner measurements for decreasing and increasing temperature. Figure 9 shows as an example the temperature dependence of the Meissner signal at $B=15$ mT. The data taken during cooling are represented by solid circles. At the lowest temperature (~ 2.1 K) the sample was kept for a few seconds during which we observed a slightly increasing diamagnetic signal. This shows that the magnetic flux which penetrates the sample is weakly trapped at pinning centers and can leave the sample at lower temperatures only slowly depending on the flux dynamics. This relaxation effect of the magnetization has been observed earlier in other organic superconductors.[3,24] For κ-(BEDT-TTF)$_2$I$_3$ we could not investigate this phenomenon in detail since the cryostat does not allow to keep temperatures constant below 4.2 K for a longer time.

During the following upward temperature sweep (open circles in Fig. 9) a clear hysteresis in the Meissner signal is observed. In this case the external field can penetrate the sample only slowly. At a characteristic temperature T_{irr}, the hysteresis vanishes and M becomes reversible which is shown by an arrow in Fig. 9. Irreversibility temperatures for different fields extracted in the depicted way are plotted in Fig. 8 as solid triangles. Close to T_c the data points lie below the values obtained from ac susceptibility but seem to merge at lower temperatures. For the experimentally accessible temperature range ($2.7\mathrm{K}<T<3.5$ K) the data points can be approximated by $B_{irr}\propto(1-t)^2$ which can be derived from (5)

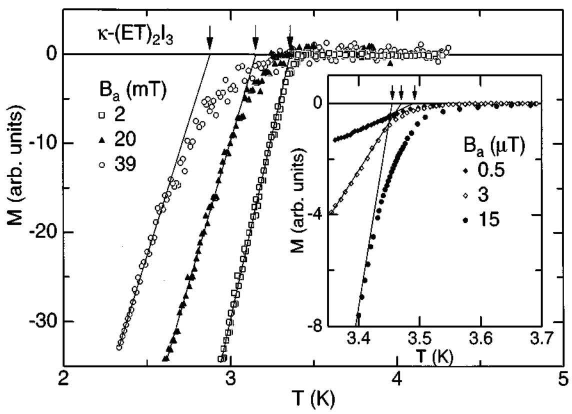

FIG. 10. Temperature dependence of the magnetization in selected fields applied perpendicular to the planes. The inset shows M for very low fields where the extrapolated T_{c2} is rapidly decreasing. The arrows indicate the critical temperatures T_{c2} which are plotted in Fig. 8.

assuming a excitation volume $V \propto a_0^2 c'$, where c' is a temperature-independent lattice parameter. The reduced values of the irreversibility fields extracted from the Meissner measurements with an approximate sweep rate of 0.2 K/min are consistent with the behavior expected according to (5) and fits within the flux-creep picture.

C. Upper critical fields

From the above presented mixed-state properties it is evident that a reliable determination of B_{c2} is possible only by measurements where fluctuation and irreversibility effects can be separated. Magnetization measurements have been used successfully both for high-T_c materials and for some organic superconductors. We determined B_{c2} and T_{c2}, i.e., the critical temperature at a fixed external field, respectively, from magnetization data as shown in Figs. 9 and 10. With decreasing T a fluctuation-induced rounded region in $M(T)$ is followed by an approximately linear region. The critical temperature T_{c2} is defined as the intercept of linear extrapolations of $M(T)$ in this superconducting region with $M=0$. This corresponds to a mean-field-like transition temperature which seems to be the most reasonable value in the present case. For the highly anisotropic high-T_c cuprates like $Bi_2Sr_2CaCu_2O_8$ it is known that this kind of analysis leads to a seemingly increasing T_c with field.[25] Several theoretical models which take into account the fluctuation effects for layered superconductors in a more quantitative way have been applied.[26,27] The theory by Koshelev[27] which is based on a GL theory for 2D superconductors including Gaussian and critical fluctuations could describe well the high-field magnetization of the layered organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br.[28] In our case, however, the magnetization curves are different from the data mentioned above as can be seen in Fig. 10. Especially, no crossing point of the magnetization curves, i.e., a field-independent M, is observed. Although κ-(BEDT-TTF)$_2$I$_3$ is expected to have a similar anisotropy this different behavior of $M(T)$ is most probably due to the lower critical field in κ-(BEDT-TTF)$_2$I$_3$ and a, therefore, larger shift of the diamagnetic onset with field (see Fig. 10).

A different kind of analysis is based on calculations by Ullah and Dorsey.[29] Thereby a scaling behavior is predicted for high enough fields where the so-called lowest Landau level approximation can be used. Indeed, this scaling analysis was applied successfully to high-T_c materials[30] and some organic superconductors.[3] For the low-field range (<60 mT) investigated here the lowest Landau level approximation is questionable. This approximation holds only in the high-field limit or for temperatures close to T_{c2}.[29] However, within error bars 2D as well as 3D scaling plots for higher fields (>1 mT) yield the same values of $B_{c2}(T)$ as the linearly extrapolated ones.

The resulting T_{c2} data are shown as solid circles in Fig. 8. For the temperature range between $2.4\ \mathrm{K} < T < 3.25\ \mathrm{K}$ the data follow roughly a linear T dependence with a slope of $\sim$ 0.061 T/K. In this temperature range B_{c2} is clearly larger than the B_{c2}^* values extracted from ac susceptibility. The magnetization data coincide nicely with $B_{c2}(T)$ determined from specific-heat measurements (open rectangles in Fig. 8).[7]

A somewhat unexpected feature is observed close to T_c. Between $3.25\ \mathrm{K} < T < 3.38\ \mathrm{K}$ a crossover of the $B_{c2}(T)$ slope with a much steeper temperature dependence is found. At higher temperatures up to T_c the slope changes again and becomes very shallow as can be seen in the inset of Fig. 8. This is similar to temperature dependences of B_{c2} reported for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (Ref. 31) and for $YBa_2Cu_3O_{7-\delta}$.[32] In Ref. 31 this behavior was interpreted as a dimensional crossover from strong anisotropy ($B_{c2\parallel}/B_{c2\perp} \equiv \gamma \approx 80$) at low temperature to a weaker one ($\gamma \approx 13$) close to T_c. In κ-(BEDT-TTF)$_2$I$_3$ this effect is even more drastic. At $3.3\ \mathrm{K} < T < T_c$ the values of $B_{c2\parallel}(T)$ extracted from our magnetization measurements (open triangles in the inset of Fig. 8) are even below $B_{c2\perp}$. This reversed anisotropy changes into the expected one at lower temperatures. $B_{c2\parallel}$ grows much faster than $B_{c2\perp}$, reaching approximately 7 T, i.e., $\gamma = 35$, at the lowest T. The values of $B_{c2\parallel}(T)$ have been extrapolated from angular dependent ac-susceptibility data as shown in Fig. 6.

The slope changes of $B_{c2}(T)$ might be an indication for a dimensional crossover. More likely, however, the theoretically not fully understood increase of fluctuations already at very low fields mimics this apparent crossover. The inset of Fig. 10 shows the temperature dependence of M for three very small fields up to 15 μT. For increasing fields the onset of the diamagnetic signal shifts clearly towards higher temperatures with a concomitant increase of the fluctuation-induced rounded region. The slopes of the linear regions (solid lines in Fig. 10) become increasingly steeper up to fields of $\sim$ 0.5 mT where the $B_{c2}(T)$ curve shows the crossover at $T \approx 3.38$ K. For higher fields we observe a clear shift of the diamagnetic onset and a decreasing slope of the linear region (see main panel of Fig. 10). For this field range the approximately linear temperature dependence of B_{c2} is found. An interesting point is that above approximately 3.38 K up to T_c the critical fields extracted from ac susceptibility are seemingly larger than the shown B_{c2} values. Finally we note that the observed strong fluctuation effects and the fast decrease of T_c already in very small fields explains the observations of the specific-heat measurements done in the earth's field where a broadened jump at the reduced critical temperature of 3.4 K was found.[7]

From the measurements described above the first estimates of the superconducting parameters taking into account the full range of measured properties on a single organic sample were made. The results are shown in Table I. The GL parameter $\kappa=\xi/\lambda$ determined by the implicit relation $B_{c1}/B_{c2}=\ln\kappa/2\kappa^2$ is ~ 7 and ~ 675 for B perpendicular and parallel to the planes, respectively. The coherence lengths and penetration depths are derived in the usual way from the critical fields and κ. The coherence length perpendicular to the planes, $\xi_\perp$, is clearly shorter than the interlayer lattice distance of approximately 1.6 nm. The penetration depth parallel to the planes for parallel fields is of macroscopic quantity ($\lambda_\parallel \approx 70\ \mu$m) which reflects the extraordinary small $B_{c1\parallel}$ and the small critical current perpendicular to the planes. It should be noted here that the qualitative features in the measured B_{c1} and B_{c2} not expected in standard Ginzburg-Landau treatment suggest that the used conventional description to obtain the superconducting parameters might be inadequate for the 2D organic superconductors.

An interesting point is the comparison of the thermodynamic critical field $B_{\rm cth}$ obtained either from magnetization or specific-heat measurements. From $B_{c1\perp}$ and $B_{c2\perp}$ a value of $B_{\rm cth}=B_{c2}/\kappa\sqrt{2}=B_{c1}\sqrt{2}\kappa/\ln\kappa\approx 20$ mT results. This coincides nicely with $B_{\rm cth}\approx 17$ mT estimated from specific-heat data.[7] For the latter value the relation for the condensation energy,

$$V_{\rm mol}\frac{B_{\rm cth}^2}{2\mu_0}=\int_0^{T_c}\Delta C\ dT, \quad (7)$$

was used. $V_{\rm mol}$ is the molar volume and ΔC is the specific-heat difference between the superconducting and normal state. On the other hand, for B parallel to the BEDT-TTF layers, $B_{cth}\approx 7$ mT, is obtained. This unphysical result must be caused by a reduced value of either $B_{c1\parallel}$ or $B_{c2\parallel}$. The latter might be possible if one takes into account the anisotropies of the sister compound κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. A value of $\gamma\approx 220$ (Ref. 33) has been reported which is considerably larger than $\gamma=35$ in the present case. The value of $B_{c2\parallel}\approx 7$ T observed here is in the range of the paramagnetic limit $B_p=1.85\times T_c$ T/K ≈ 6.5 T.[34] This might be an indication for a possible reduction of $B_{c2\parallel}$ due to this pair-breaking limit and would prove the conventional s-wave pairing of Cooper pairs in the superconducting state. Another possibility to account for the reduced value of the thermodynamic critical field might be a reduced $B_{c1\parallel}$ due to the 2D layered structure which in the extreme case results in Josephson-coupled individual layers. The extracted $B_{c1\parallel}$ then measures the critical field for the Josephson currents rather than the thermodynamic value. However, the stated values of $B_{c1\parallel}$ might be even too large since a small misalignment ($\sim 2°$) of the sample might have been possible in the magnetization measurements.

IV. SUMMARY

We have presented the first thorough study of the superconducting parameters of κ-(BEDT-TTF)$_2$I$_3$ in the whole superconducting temperature-field range. Thereby we took into account all the unusual behavior now known to occur in weakly pinned anisotropic superconductors. ac-susceptibility and high-resolution low-field SQUID magnetization measurements have been utilized to determine the upper and lower critical fields and to study irreversibility effects in the mixed state. From $T_c=3.5$ K down to $T/T_c\approx 0.86$, $B_{c1\perp}$ is strongly suppressed to a value below the experimental resolution. This feature seems to be common to 2D layered superconductors and might be qualitatively understood by single-vortex fluctuations. Quantitatively, however, the observed effect is at least an order of magnitude too large. For fields parallel to the layers no such suppression of the lower critical field was observed.

The upper critical fields B_{c2} seem to be reduced close to T_c as well, however only down to $T/T_c\approx 0.97$. Thereby the exact determination of the critical temperature in magnetic fields is hampered due to the quickly increasing fluctuation-induced rounding of the magnetization curves already in very small external fields. A detailed theoretical understanding of the magnetization for layered superconductors in this field range is missing.

The critical field B_{c2}^* extracted from ac-susceptibility data revealed a perfect 2D angular dependence. This critical field, however, is rather a measure of a particular irreversibility field which depends on the detailed nature of the flux-line dynamics in the sample. The frequency and temperature dependence of B_{c2}^* fits with the existing flux-creep models.

From the critical field data a complete set of superconducting parameters is derived. Good agreement between the thermodynamic critical fields determined from perpendicular critical fields and from specific-heat data is found. However, a clear discrepancy exists to the value extracted from the critical fields for the parallel direction. This might be understood by a possibly reduced value of $B_{c2\parallel}$ which may be caused by the magnetic pair breaking of the Cooper pairs. Further studies are needed to elucidate the complex superconducting state of the layered organic superconductors.

ACKNOWLEDGMENTS

Many useful discussions with H. v. Löhneysen are gratefully acknowledged. This work was supported by the Deutsche Forschungsgemeinschaft.

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