Critical state and lower critical field of the organic superconductor $\varkappa$-(BEDT–TTF)$_2$Cu(NCS)$_2$

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The static diamagnetic susceptibility of single-crystal $\varkappa$-(BEDT–TTF)$_2$Cu(NCS)$_2$ in the superconducting state were measured. The critical field $H_{c1}^{\perp}(T)$ and the critical magnetization current $J_c(T)$ in weak magnetic fields were determined with allowance for the sample shape and for the bulk pinning. The possible causes of the deviation of the observed $H_{c1}^{\perp}(T)$ dependence from that predicted by the BCS theory are discussed. The London penetration depth and the Ginzburg–Landau parameter are estimated at $\lambda^{\parallel}(0) \approx 1500$ Å and $\varkappa(0) \approx 8.1$.

The organic superconductor $\varkappa$-(BEDT–TTF)$_2$Cu(NCS)$_2$ has a critical temperature[1] $T_c \approx 10$ K at atmospheric pressure, the present record for organic metals. The measured dynamic[2,3] and static[1,4,5] susceptibilities point to a volume-dependence of the superconductivity in this compound.

The lower critical field H_{c1} was estimated in a number of studies[3–6] from measurements of the magnetic moment. It should be noted that the experiments of Refs. 3 and 4 were made on polycrystalline samples. It is difficult in this case to take into account the strongly anisotropic character of the investigated substance. Anisotropic-superconductor properties, such as the critical field, are obviously best studied in single crystals, as was done in Refs. 5 and 6. In Ref. 5 the value of $H_{c1}^{\perp}$ at $T = 4.2$ K was determined by observing the start of the deviation of the field dependence of the sample magnetization $M(H)$ from linearity, and amounted to 1.5 Oe (without allowance for the demagnetizing factor). Plots of $M(H)$ in the temperature range 5–8 K were obtained in Ref. 6, where $H_{c1}^{\perp}$, determined just as in Ref. 5, was found to be ≈ 25 Oe at $T \approx 5$ K. So large a difference between the estimates of H_{c1} may be due to the influence of the magnetizing factor, and also to differences in the quality and shape accuracy of the samples. Indeed, the presence of "weak spots" in the sample (such as acute angles or small nonuniformity of T_c in the sample) can greatly lower the field corresponding to the start of penetration of the magnetic flux compared with the value of H_{c1} in a bulky sample. An uncertainty in the estimate of H_{c1} from the start of the deviation of $M(H)$ from linearity is introduced also by Abrikosov-vortex pinning that delays the penetration of the flux into the sample.

Our aim was an experimental study of the static diamagnetic susceptibility of single-crystal $\varkappa$-(BEDT–TTF)$_2$Cu(NCS)$_2$ in the superconducting state, as well as an estimate of the lower critical field H_{c1} and the critical magnetization current J_c with allowance for the shape of the sample and the bulk pinning of the magnetic flux.

The $\varkappa$-(BEDT–TTF)$_2$Cu(NCS)$_2$ single crystals were obtained by electrochemical oxidation of BEDT–TTF in 1,2-trichlorethane (at a concentration $2\cdot 10^{-3}$ mol/l), using dc current ($I = 1.15\,\mu$A) and a platinum electrode at a constant temperature 20 °C. The electrolyte was a Cu(SCN)–K(SCN) complex prepared immediately before the synthesis in an electrochemical cell by dissolving Cu(SCN) ($5\cdot 10^{-3}$ mol/l) in the presence of K(SCN) and the cyclic ester 18-crown-6 in a ratio 1:1:1.

The measurements were performed on a $\varkappa$-(BEDT–TTF)$_2$Cu(NCS)$_2$ single crystal measuring $0.88\times 0.15\times 0.03$ mm in an external field from 0.1 to 40 Oe at temperatures from 2 to 10 K. Preliminary resistive measurements have shown that the sample becomes superconducting at $T_c \approx 10.2$ K (a value determined from the center of the resistive transition), and the resistance vanished completely at $T \approx 8.8$ K. To measure the magnetic moment we used a magnetometer based on an hf SQUID. The magnetometer was calibrated against lead and tin references with dimensions close to those of the sample. The sample diamagnetic screening signal agreed with the signal from the references within $\approx 10\%$.

Figure 1 shows the temperature dependences of the magnetic susceptibility of the sample at different values of the magnetic field H_{ext} directed perpendicular to the *bc* crystal plane. Curves 1, 2, and 3 correspond to diamagnetic screening (zero field cooling), and 1′,2′,3′ to crowding out of the magnetic flux, the Meissner effect (field cooling). In fields $H_{ext} \leqslant 1$ Oe the Meissner effect is $\geqslant 40\%$ of the total diamagnetic-screening signal, in agreement with data by others.[5,6] When the field is increased, the relative fraction of the Meissner effect is decreased, and starting with ~ 15 Oe the absolute value of the magnetic flux crowded out of the sample saturates and ceases to depend on the field.

When the external field was directed along the conduct-

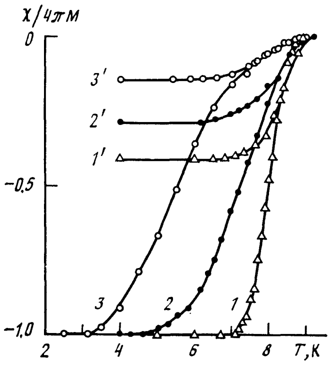

FIG. 1. Temperature dependence of the magnetic susceptibility in the case of diamagnetic screening (curves 1,2,3) and the Meissner effect (curves 1′,2′,3′) in a field $H \perp bc$. Curves 1 and 1′ correspond to an external field $H_{ext} = 1.2$ Oe, 2 and 2′ to $H_{ext} = 5.4$ Oe, and 3, 3′ to $H_{ext} = 16.5$ Oe.

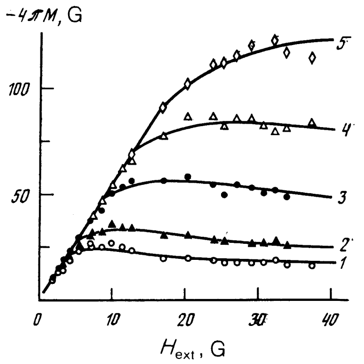

FIG. 2. Plots of the average sample magnetization on an external field $H \perp bc$ at temperatures: *1*—$T = 6.5$ K; *2*—6.0 K; *3*—5.0 K; *4*—4.0 K; *5*—3.0 K. The solid curves were computed (see the text).

ing *bc* plane of the crystal, the superconducting transition was smeared, from ≈ 9 to ≈ 3 K even at $H \sim 2$ Oe, meaning a low value of the critical field in this plane, i.e., strong anisotropy of H_{c1} for this substance. The fraction of the Meissner effect at $H \parallel bc$ was less than 5%.

Figure 2 shows typical magnetization curves $M(H)$ in a field $H \perp bc$ for various temperatures. The curves were obtained from the initial temperature dependences of the screening signal. Since comparison with the standards has shown that in the superconducting state the sample screening is complete, the slope of the initial linear sections was assumed to be $-4\pi M/H_{ext} = (1 - D_0)^{-1}$, where $D_0 = 0.826$ is the demagnetizing factor calculated assuming the sample to be ellipsoidal. At sufficiently high values of the field the dependence of the magnetization on the field reaches saturation: $4\pi M = 4\pi M_c(T)$. This behavior is typical of type-II superconductors with strong pinning, and is described by the critical-state model.[7,8]

According to this model the magnetic-field distribution in a magnetized long cylindrical type-II superconductor takes the form shown in Fig. 3a. The change of the magnetic induction in the region where the bulk screening currents flow is determined by the critical current J_c, above which the Abrikosov vortices become detached with the pinning center and move into the interior of the sample: curl $\mathbf{B} = -(4\pi/c)\mathbf{J}_c$. The critical current can be assumed to be independent of the field in a small field interval near H_{c1}. Under this assumption, the critical current is easily determined from the saturation magnetization of a cylinder in a parallel field[7]: $J_c = -3cM_c/R$, where R is the cylinder radius. For a sample in the form of a three-axis ellipsoid with semi-axes $\alpha, \beta, \gamma (\alpha > \beta > \gamma)$ in a field parallel to the shortest axis γ, the expression for J_c takes the form

$$J_c = \frac{32c}{9\pi}\frac{\alpha}{\beta^2}\left(\frac{\alpha-\beta}{2\beta}+\frac{1}{3}\right)^{-1} M_c. \quad (1)$$

A similar magnetic-flux penetration picture should be observed also when the sample is heated in a constant external field from low temperatures to $T > T_c$ (Fig. 3b). The values of J_c and H_{c1} are of course temperature dependent, but for given T the magnetic-flux distribution must coincide with that for the sample magnetized at this temperature. Therefore the curves of Fig. 2 can be regarded, in the model considered, as equivalent to the $M(H)$ curves obtained directly from magnetization experiments.

Simple analytic expressions for the field dependence of the average magnetization of a long sample in a parallel field were obtained in Refs. 7 and 8 for the field dependence of the average magnetization at $H_{c1} < H < H^*$ (H^* is the field at which the magnetization begins to saturate). In the case of a thin plate, which our sample is in fact, the demagnetizing factor must be taken into account in a transverse field. We can assume a demagnetization factor $D \equiv D_0$ for weak penetration of the field into the plate ($D_0 = 0.826$ for this particular sample), and substitute $H = H_{ext}/(1 - D_0)$ in the expression for $M(H)$ (Refs. 7,8).

If the flux penetration is appreciable, it is necessary to take into account the inhomogeneity of the induction $B(\mathbf{r})$ inside the sample, and the above simple substitution becomes invalid. To find the functions $M(H)$ in this case we must numerically compute directly the magnetic moment produced by the screening currents induced in the sample by the external field. We chose as the basis for such a computation the above-described Bean model of field penetration (Fig. 3). The total magnetic moment can then be taken to equal the sum of the moments of the "Meissner" region (region with $B = 30$) and of the bulk screening currents outside this region. The sample was assumed to be macroscopically uniform, and the critical current to be isotropic in the *bc* plane. The sample shape was approximated by a three-axis ellipsoid. It was assumed in addition that the "Meissner" region is also an ellipsoid.

The fitting parameters in the comparison of the calculated $M(H_{ext})$ curves with the experimental ones are H_{c1} and M_c. The results of the fitting are shown by the solid lines

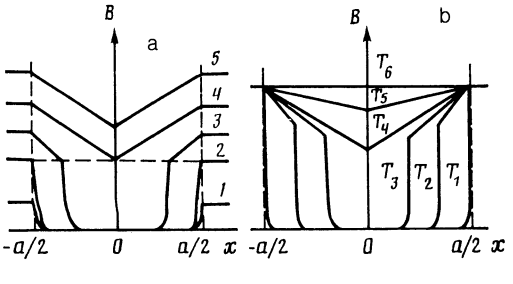

FIG. 3. Penetration of a magnetic field into a long cylindrical sample of diameter a in the critical-state model.[7,8] a—Sample magnetization at constant temperature: *1*—$H_{ext} < H_{c1}$; *2*—$H_{ext} = H_{c1}$; *3*—$H_{c1} < H_{ext} < H^*$; *4*—$H_{ext} = H^*$, *5*—$H_{ext} > H$. b—Sample heating in a constant field: $T_1 < T_2 < T_3 < T_4 < T_5 < T_6 = T_c$.

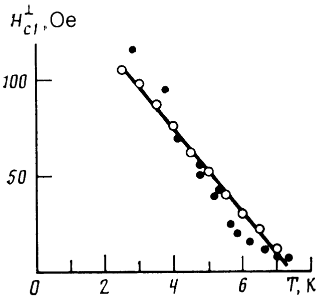

FIG. 4. Temperature dependence of lower critical field $H_{c1}^{\perp}$: ○—calculated points; ●—points corresponding to 5% deviation of the $M(T)$ dependence on the total diamagnetic signal.

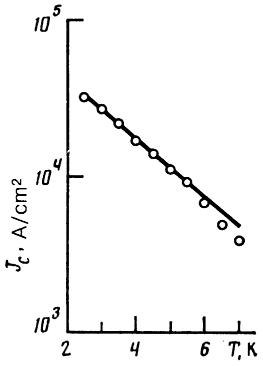

FIG. 5. Temperature dependence of the critical current in the bc plane in a field close to H_{c1} and perpendicular to this plane.

of Fig. 2. The values of $H^{\perp}_{c1}(T)$ obtained in this manner are shown in Fig. 4 and are well approximated by a linear temperature dependence in the entire investigated temperature interval. The derivative is $dH^{\perp}_{c1}/dT = -21.5$ Oe/K, and the value of $H^{\perp}_{c1}(0)$ obtained by extrapolating the linear dependence to $T = 0$ K is ≈ 160 Oe. This corresponds to a penetration depth $\lambda^{\parallel}(0) \approx 1500$ Å and to a Ginzburg–Landau parameter $\varkappa^{\parallel}(0) \approx 8.1$.

There is at present no clear-cut theoretical basis for the linear temperature dependence of $H_{c1}(T)$ in a wide range of temperatures all the way to $T \sim 0.3T_c$. The observed deviation from the known dependence of the BCS theory can possibly be attributed to peculiarities of the scattering in this particular substance. Indeed, if the electron mean free path $l(T)$ is calculated from the electric resistivity $\rho(T)$ using the relation

$$l(T) = 12\pi^3\hbar/[\rho(T)e^2S],$$

where S is the corresponding area of the intersection with the Fermi surface (data[9] on the Shubnikov–de Haas oscillations yield the estimate $S \approx 6.3 \cdot 10^{15}$ cm^{-2}), we obtain by substituting $\rho(10) \sim 2.5 \cdot 10^{-4}$ Ω cm the value $l(10\text{ K}) \approx 100$ Å, which is comparable with coherence length[10] $\xi^{\parallel}(0) = 182$ Å. It can consequently influence noticeably the effective penetration depth (at $l \ll \xi$, $\lambda = \lambda_0(\xi_0/l)^{1/2}$). Note that the resistance of $\varkappa$-(BEDT–TTF)$_2$Cu(NCS)$_2$ crystals does not saturate ahead of the superconducting transition, but continues to depend strongly (approximately quadratically) on the temperature. A quadratic temperature dependence of the resistance is observed also for other metals based on BEDT–TTF (Ref. 11) and is attributed to strong electron–electron scattering. This dependence should lead to an initial growth of the mean free path when the temperature drops below T_c. As a result, when cooled from $T = T_c$ to $T = 0$ K the substance can go over from the "dirty" regime ($l < \xi_0$) to the "clean" one ($l > \xi_0$). This leads to an $H_{c1}(T)$ dependence stronger than dependence in BCS theory (Ref. 12).

Figure 4 shows also points corresponding to the start of vortex penetration into the sample [at 5% deviation of the $M(T)$ curve from the total diamagnetic signal in the corresponding field], with allowance for the demagnetizing factor D_0. For these points the field dependence becomes ever steeper when the temperature is lowered. This is most likely due to enhancement of the vortex pinning. In fact, the critical fields calculated by Eq. (1) from the corresponding values of M_c exhibit below 6 K a nearly exponential dependence (Fig. 5): $J_c = J_{c0}\exp(-\alpha T)$, where $\alpha \approx 0.43$ K^{-1} and $J_{c0} \approx 10^5$ A/cm^2.

We note in conclusion that similar temperature dependences of the lower critical field and of the critical magnetization current are observed also in high-temperature superconductors.[13,14] One cannot exclude the possibility that they are due to some peculiarities common to these compounds, say the layered character of their structure or a strong electron–phonon interaction.

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[1]H. Urayama, H. Yamochi, G. Saito, *et al.*, Chem. Lett. **55** (1988).
[2]S. Gartner, E. Gogu, I. Heinen, *et al.* Solid State Commun. **65**, 1531 (1988).
[3]T. Sugano, K. Terui, S. Mino, *et al.* Chem. Lett., 1171 (1988).
[4]L. I. Buravov, A. V. Zvarykina, N. D. Kushch, *et al.*, Zh. Eksp. Teor. Fiz. **95**, 322 (1989) [Sov. Phys. JETP **68**, 182 (1989)].
[5]H. Veith, C.-P. Heidmann, H. Muller, *et al.*, Synth. Met. **27**, A361 (1988).
[6]M. Tokumoto, H. Anzai, K. Takahashi, *et al.*, *ibid.* **27**, A305 (1988).
[7]C. P. Bean, Phys. Rev. Lett. **8**, 250 (1962).
[8]C. P. Bean, Rev. Mod. Phys. **36**, 31 (1964).
[9]K. Oshima, T. Mori, H. Inokuchi, *et al.*, Phys. Rev. B **38**, 938 (1988).
[10]K. Oshima, H. Urayama, H. Yamochi, and G. Saito, J. Phys. Soc. Jpn. **57**, 730 (1988).
[11]L. N. Bulaevskiĭ, V. B. Ginodman, A. B. Gudenko, *et al.*, Zh. Eksp. Teor. Fiz. **94**, No. 4, 285 (1988) [Sov. Phys. JETP **67**, 810 (1988)].
[12]A. A. Golubov, O. V. Dolgov, and A. B. Koshelev, Solid State Commun. **71**, 1989.
[13]M. V. Kartsovnik, V. A. Larkin, V. V. Ryazanov, N. S. Sidorov, and I. F. Shchegolev, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 595 (1988) [JETP Lett. **47**, 691 (1988)].
[14]S. Senoussi, M. Oussena, G. Collin, and I. A. Campbell, Phys. Rev. B **37**, 9792 (1988).

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