Critical fields, magnetization curves, and flux creep of single crystals of the organic superconductor k-$(BEDT-TTF)_2Cu[N(CN)_2]Br$

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(Submitted 9 December 1991)
Zh. Eksp. Teor. Fiz. **101**, 1945–1953 (June 1992)

We have studied the field and temperature dependences of the critical current density in k-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ single crystals and determined the magnitude of the critical-current anisotropy in the limit $B \to 0$ at $T = 2.1$ K. We investigated the relaxation of the magnetic moment and determined the average activation energy of Abrikosov vortices $U_0 \approx 7$ meV.

INTRODUCTION

A new organic superconductor based on BEDT-TTF with the anion $Cu[N(CN)_2]Br$ was synthesized at the Argonne National Laboratory a little more than one year ago.[1] Among organic superconductors, the cation-radical salt k-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ still has the highest superconducting temperature $T_c \sim 12$ K (Refs. 1–3) at normal pressure. The magnetic properties of this superconducting compound have still not been studied. For this reason, in the present work we used a SQUID magnetometer[4] in the range of magnetic fields ± 0.3 T and in the temperature range 2–15 K to study the magnetization curves, the temperature and field dependences of the critical current density, and the magnetization relaxation.

EXPERIMENTAL RESULTS

Sample preparation and experimental procedure

Single crystals of k-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ were prepared by electrochemical oxidation of BEDT-TTF (concentration $C_1 = 2 \cdot 10^{-3}$ moles/liter) in 1,1,2-trichloroethane (to which 2% absolute ethanol was added) at a platinum anode in the dc current regime ($I = 0.5\ \mu$A). The electrolyte consisted of the complex 18-crown-6 with $NaN(CN)_2$ and CuBr, taken in the ratio 1:1:1 ($C_2 = 2 \cdot 10^{-3}$ moles/liter). Two crystals with the following characteristic dimensions were selected from the series of single crystals for further measurements: $0.75 \times 0.68 \times 0.05$ mm^3 (crystal No. 1) and $0.68 \times 0.50 \times 0.13$ mm^3 (crystal No. 2). The samples were mounted on the sidewall of a quartz ampul and the ampul was evacuated, sealed, and filled with spectrally pure helium to a pressure of ~ 20 Torr (Ref. 4). In the measurement of the relaxation of the magnetic moment the magnetic field induction rate was equal to ~ 1–10 T/s, and in the measurements of the magnetization curves the field was scanned with a rate of $dB_e/dt \approx 10^{-4}$ T/s.[4]

Temperature dependence of the magnetic moment P_m

The temperature dependence of the magnetic moment of the single crystals k-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ Nos. 1 and 2, prepared in the ZFC regime (cooling in zero magnetic field $\sim 10^{-5}$ T, followed by induction of the field B) and FC regime (cooling in a field B), is displayed in Fig. 1; the curves were obtained in a magnetic field $B = 3.5$ mT with the orientation $B \perp bc$. The difficulty of determining T_c from the magnetization curves should be noted: in the normal state the k-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ single crystals are weakly diamagnetic and the transition into the superconducting state is accompanied only by an increase in the diamagnetic moment P_m and not by a change in sign, as, for example, happens in $Y_1Ba_2Cu_3O_x$ single crystals. Since the exact form of the temperature dependence $P_m^{ZFC}(T)$ is not known (see inset in Fig. 1), the value of T_c will depend on the threshold sensitivity ΔP_m of the determination. It is this factor that apparently explains the difference in the value of T_c determined from the resistance measurements and from the susceptibility [$R(T)$ gives the upper limit and $\chi(T)$ gives the lower limit]. We also note that the field $B = 3.5$ mT at $T = 2$ K is higher than the first critical field for the orientation $B \perp bc$; this is also confirmed by the field dependence of $P_m^{ZFC}(B)$ for this temperature.

Field dependence of the magnetic moment

The magnetization curves of k-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ single crystals at different temperatures in the orientation $B \perp bc$ (bc is the conducting plane of the crystal) are presented in Fig. 2. The magnetization curves have the form characteristic for type-II soft superconductors. As the temperature increases the width of the

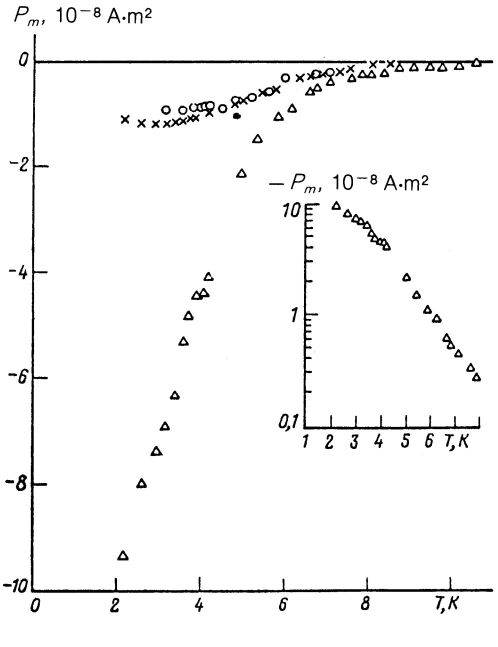

FIG. 1. Temperature dependence of the magnetic moment of k-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ single crystals for the orientation $B \perp bc$: Δ—ZFC, $B = 3.5$ mT, crystal No. 1; ○—FC, $B = 3.5$ mT, crystal No. 1; ×—ZFC, $B = 3.5$ mT, crystal No. 2.

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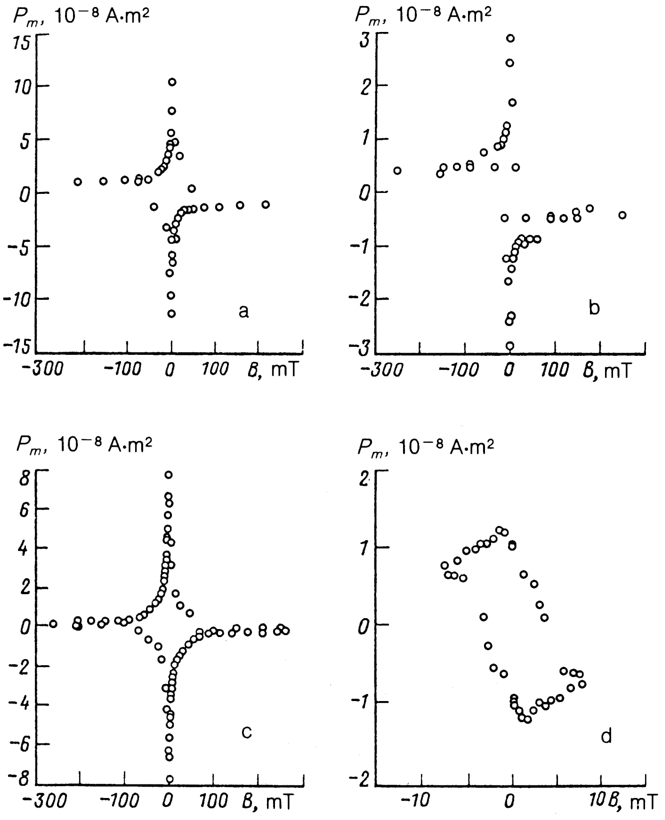

FIG. 2. Magnetization curves of a k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystal for the orientation $B \perp bc$ (bc is the conducting plane of the crystal): a) $T = 2.1$ K, crystal No. 1; b) $T = 4.2$ K, crystal No. 1; c) $T = 6.5$ K, crystal No. 1; d) $T = 4.2$ K, crystal No. 2.

hysteresis loop decreases, but for this orientation, although the demagnetization factor $n \approx 0.9$ is significant, the P_m^{ZFC} (B) curves do not become reversible below $T \sim 7.5$ K. The maximum on the magnetization curve P_m^{ZFC} (B) for $B \perp bc$ can be associated with the field B^* in which the screening currents first reach the center of the sample.[5,6] Since the sample is nearly a square plate,

$$H^* = \frac{2^{1/2} j_c t}{\pi} \ln(2\alpha L/t), \qquad (1)$$

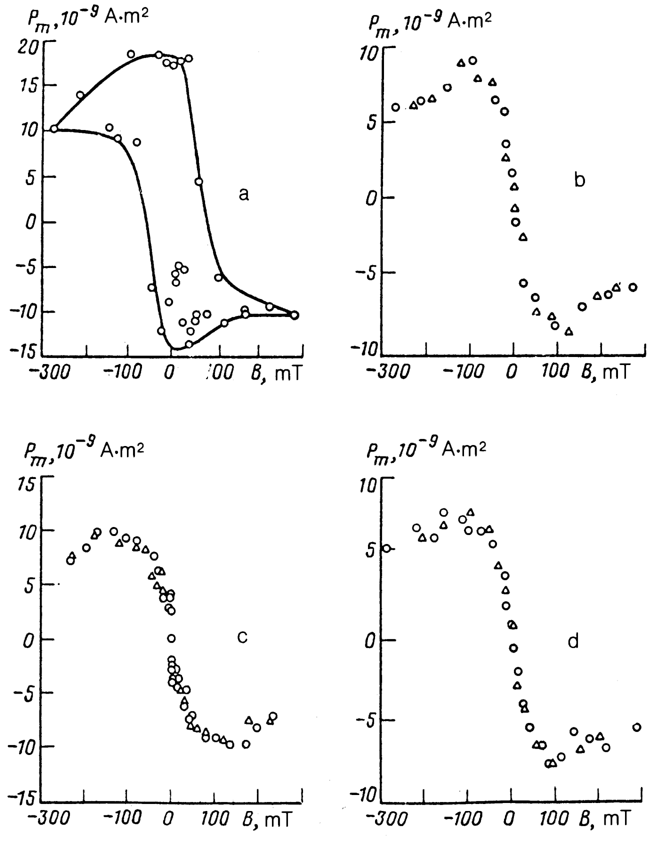

FIG. 3. Magnetization curves of a k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystal for the orientation $B \parallel bc$ (crystal No. 1): $T = 2.1$ K (a), 4.2 K (b), 5.7 K (c), and 7.1 K (d). ○ for b,c,d corresponds to the increase of B, and △ corresponds to its decrease.

where L is the edge length of the plate, t is the thickness of the plate, and $\alpha \approx 1.105$ (Ref. 6). Substituting the value of j_c at $T=2$ K we obtain $H^* \approx 1.1$ Oe, which agrees quite well with the experimental value. We also note that when the j_c (B) dependence is taken into account the maximum in P_m (B) is observed in fields weaker than H^*.

For the orientation $B \parallel bc$ (the field lies in the plane of the crystal) the $P_m^{\rm ZFC}$ (B) are completely reversible even at the temperature $T=4.2$ K (Fig. 3), and they do not change significantly with increasing temperature. The reversibility of the magnetization curves indicates that, to within the accuracy of measurement ($\Delta P_m \sim 10^{-10}$ A·m^2), for this orientation (between the conducting layers) and temperature there are no screening currents.

In this case the magnetization curve is determined by the elasticity of the vortex lattice[6] and the magnitude of the surface barrier,[7] and the latter contribution apparently dominates. This follows from the following simple considerations. Since

$$H_{c1} = \frac{\Phi_0}{4\pi\lambda_i\lambda_k}\left[\ln\frac{(\lambda_i\lambda_k)^{1/2}}{(\xi_i\xi_k)^{1/2}}\right], \qquad (2)$$

where Φ_0 is the magnetic-flux quantum, λ is the penetration depth in a direction perpendicular to the magnetic field, and ξ is the component of the anisotropic coherence length.[8] Taking the values of these parameters from Refs. 3 and 9 and assuming λ to be practically isotropic in the plane of the crystal with $H \perp bc$,[9] we obtain $H_{c1}{}^{\perp}(0) = 3.1 \cdot 10^{-3}$ T and $H_{c1}{}^{\parallel}(0) = 1.4 \cdot 10^{-3}$ T, where the first quantity is the first critical field of the crystal for the orientation $B \parallel bc$ and the second one is the critical field for $B \perp bc$. If $H_{c1}^{\perp}$ (0) agrees in order of magnitude, taking into account the demagnetization factor $N \approx 0.9$ and the temperature dependence $H_{c1}^{\perp}$ (T), with the experimental value, which for soft type-II superconductors is close to the value H_t corresponding to the maximum of $P_m^{\rm ZFC}$ (H) (see Fig. 2a), then we obtain for $H_{c1}^{\perp}$ a value that is at least an order of magnitude smaller than the field H_t at which the maximum $P_m^{\rm ZFC}$ is observed (Figs. 3b and c). Hence we conclude that the surface barrier makes a significant contribution to the magnetization curve, though in this case it is difficult to explain the reversibility of the magnetization curve (Figs. 3b and c).

Critical current densities

The temperature and field dependences of the critical current density j_c were determined, on the basis of Bean's anisotropic model (see, for example, Ref. 6), from the irreversible parts of the magnetization curves for k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystals (Figs. 2 and 3). The temperature dependence j_c (T) for the orientation $B \perp bc$ for the single crystals 1 and 2 is described by the relation

$$j_c(T,\ 0) = j_c(0,\ 0)\exp(-T/T_0) \qquad (3)$$

with $j_c\,(0,0) \approx (1\text{–}1.2) \cdot 10^4$ A/cm^2 and $T_0 \approx 1.2$–1.4 K (see Fig. 4). The quantity j_c (0,0) is of the same order of magnitude as j_c (0,0) for another organic superconducting single crystal k-(BEDT-TTF)$_2$Cu(NCS)$_2$ (Ref. 10). We note that the temperature dependence j_c (T) can also be represented in the form (3) for $B \neq 0$ (see inset in Fig. 1). At low temperatures ($T < 3$ K) some deviation is observed from the relation (3) for both crystals. The magnitude of the anisotropy of the critical currents is $K = j_c^{\perp}/j_c^{\parallel} \approx 67$ as $B \to 0$, $T = 0$ K. This is significantly smaller than K for k-(BEDT-TTF)$_2$Cu(NCS)$_2$ single crystals, where $K \approx 160$ (Ref. 10).

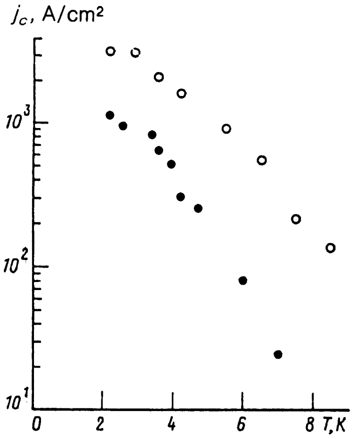

FIG. 4. Temperature dependence of the critical current density in k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystals for the orientation $B \perp bc$, $B \to 0$; ●—crystal No. 2, ○—No. 1.

The field dependence j_c (B) for different temperatures T is presented in Fig. 5. For the temperatures investigated two significantly different sections can be distinguished in the dependences j_c (B). The first section ($B \geqslant 20$ mT) has an exponential field dependence

$$j_c(B,\ T) = j_c(0,\ T)\exp(-B/B_0) \qquad (4)$$

and on the second section the field dependence j_c (B) is sharper. This form of the field dependence can probably be explained by the presence of a large number of shallow pinning centers of different depth. A small increase in the magnetic field results in detachment of vortices from the pinning centers, which in turn results in sharp damping of the current, after which the pinning centers no longer affect the

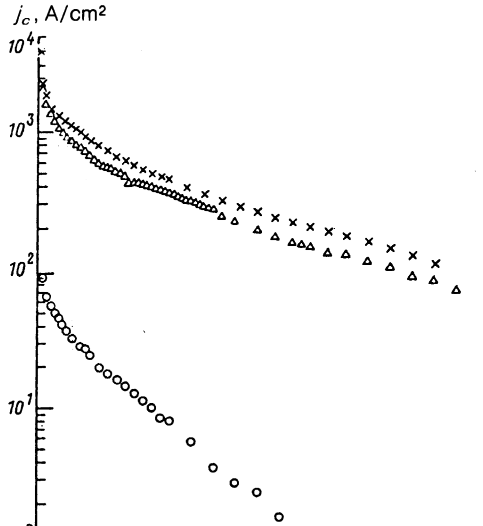

FIG. 5. Field dependence of the critical current density in k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystals (No. 1) for the orientation $B \perp bc$: $T = 2.1$ K (×), 4.2 K (△), and 6.5 K (○).

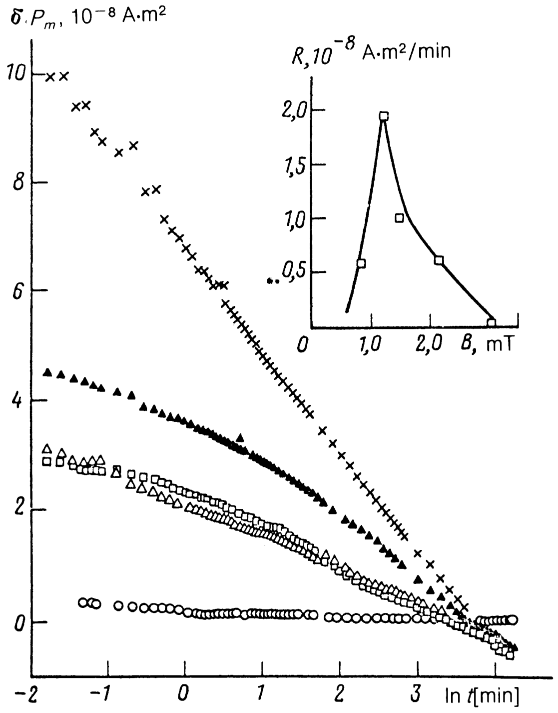

FIG. 6. $\delta P_m = P_m(t) - P_m(2000\ \text{s})$ versus ln t for a k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystal (No. 1) in the orientation $B \perp bc$ at $T = 4.2$ K. $B = 1.18$ mT (×), 0.83 (△), 2.15 (□), 3.04 (○), and 1.47 (▲). The inset shows the field dependence of the logarithmic relaxation rate $R = dP_m/d(\ln t)$ for single crystal No. 1, $B \perp bc$.

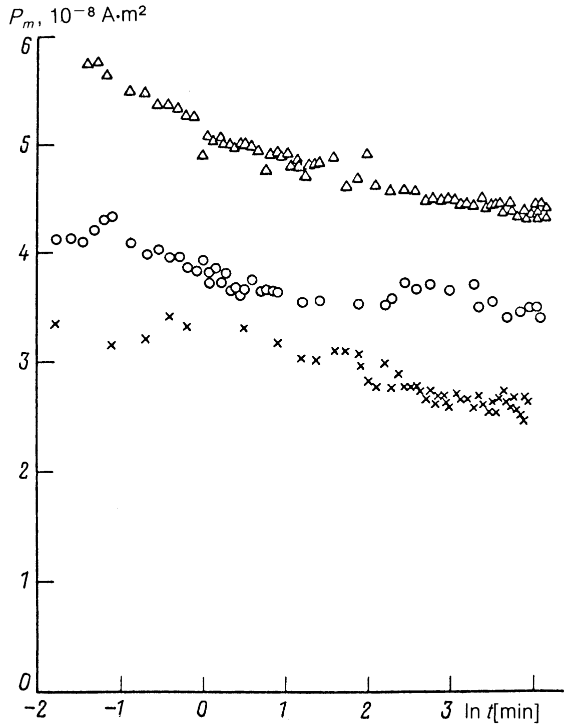

FIG. 7. Time dependence of the magnetic moment P_m of single crystal No. 2 k-(ET)$_2$Cu[N(CN)$_2$]Br at $B = 3$ mT (△), 4.6 (○), and 7.6 (×).

current, which in fields $B \geqslant 20$ mT is probably determined by the intrinsic pinning.

Time dependence of the magnetic moment

The time dependences of the magnetic moment P_m^{ZFC} in different magnetic fields were obtained for k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystals (Fig. 6). It was shown that at $T = 4.2$ K the function $P_m = f(\ln t)$ describes the behavior of P_m well only for fields $B < 3$ mT. The logarithmic relaxation rate $R = dP_m/d(\ln t)$ has a sharp peak at fields $B \sim 1$mT (see inset in Fig. 6), which correspond to a total-penetration field $B^* \approx 1.1$ mT (Ref. 6). The activation energy $U_0 \approx 7$ meV was obtained in fields $B > B^*$ and $T = 4.2$ K. Similar results were obtained in Ref. 2 for $T = 6$ K.

At times $t < 10$–10^2 s and in inceasing field ($B > 1.18$ mT) the time dependence $P_m(t)$ deviates significantly from a logarithmic dependence. Since

$$P_m(t) = P_{m_0} - R\ln(1 + t/\tau), \tag{5}$$

where P_{m_0} is the initial value of $P_m(t)$ and R is the logarithmic relaxation rate,[11] the deviation from a logarithmic time dependence at short times arises because the times t and τ are comparable. Thus τ is a macroscopic quantity and for the k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br single crystal $\tau \sim 10$–10^2 s for the given temperature. The significant deviation of P_m from a logarithmic time dependence at short times could also be due to an increase in the induction rate, $\tau = \tau(B, \partial B/\partial t)$ (Ref. 12).

Here we call attention to some features of the present series of measurements. These features are governed by the structure of the apparatus employed. The magnetic field in our SQUID magnetometer is generated by a combination of a superconducting solenoid and a niobium-titanium tube, which screens the working volume when the magnetic field of the solenoid is changing and stabilizes the field during the measurements. The high inductance of the solenoid limits the scan rate of the field ($dB_e/dt \sim 10^{-4}$ T/s), but the induction time in the working volume is significantly shortened (1–10^2 T/s) by heating the Nb-Ti tube along the generatrix ($t^* \sim 2$ ms). Thus when the relaxation of the magnetic moment in different fields is measured not only the magnitude of the applied magnetic field but also the induction rate $\partial B/\partial t$ changes, since t^* remains constant. For fields in the range 0.83–3 mT the induction rate more than triples, which apparently can also explain the appearance of significant deviation from ln t at short times.

As the magnetic field is increased further ($B > 3$ mT) the time dependence of P_m deviates significantly from logarithmic in the entire range of times employed, 3–4000 s (Fig. 7). Significant jumps are observed in the time dependence $P_m(t)$. These jumps are probably caused by detachment of large bundles of vortices from pinning centers.[13] The spread in the quantity ΔP_m indicates that the number of flux lines in such a bundle is a random quantity.

In conclusion we note that the collective-creep model ($d \ln P_m/d \ln t$) cannot explain the time dependence of P_m in the time intervals employed (up to 4000 s).[14,15]

RESULTS AND CONCLUSIONS

1. The magnetization curves for the single crystal k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br were observed to be anisotropic. For the orientation $B \| bc$ the curves $P_m^{\text{ZFC}}(B)$ for $T \geqslant 4.2$ K are practically reversible (to within the accuracy of the measurements of the magnetic moment $\Delta P_m \sim 10^{-10}$ A·m²).

2. The temperature dependence of the critical current

density for the orientation $B\perp bc$ can be described by the relation

$$j_c(B, T) = j_c(0, T)\exp(-T/T_0)$$

with $j_c(0,0) \approx (1–1.2)\cdot 10^4$ A/cm^2 and $T_0 \approx 1.2–1.4$ K.

3. The critical-current anisotropy satisfies $K = j_c^{\perp}/j_c^{\parallel} \approx 67$ as $B\to 0$ and $T = 0$ K.

4. At times $t \leqslant 10–10^2$ s and in stronger fields ($B > 1.18$ mT) and (or) higher induction rates $1–10^2$ T/s the time dependence $P_m(t)$ deviates significantly from a logarithmic dependence.

5. The logarithmic relaxation rate at $T = 4.2$ K has a sharp peak in the field B^* corresponding to the field at which the screening currents penetrate to the center of the sample. The average activation energy of Abrikosov vortices was determined to be $U_0 \approx 7$ meV.

It is our duty to thank A. A. Zhukov for helpful remarks which he contributed in a discussion of the results.

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Translated by M. E. Alferieff