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Scaling Behavior and Hall Conductivity of Mixed-State Hall
Effect in Heavy-Ion Irradiated $\text{YBa}_2\text{Cu}_3\text{O}_7$ Crystals*

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Scaling Behavior and Hall Conductivity of Mixed-State Hall Effect in Heavy-Ion Irradiated $\text{YBa}_2\text{Cu}_3\text{O}_7$ Crystals

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The Hall effect(ρ_{xy}) and longitudinal resistivity(ρ_{xx}) measured in $\text{YBa}_2\text{Cu}_3\text{O}_7$ crystals before and after the irradiation of Sn and Xe ions. We found a clear evidence that the strong pinning induced by the columnar defects not only modifies the scaling behavior between the Hall resistivity ρ_{xy} and longitudinal resistivity ρ_{xx} but also affects the temperature dependence of the Hall conductivity. For the irradiated crystals with columnar defects, the scaling exponent β of $\rho_{xy} = A\rho_{xx}^\beta$ was found to be $\beta = 1.55 \pm 0.1$, whereas β of the unirradiated one was larger than 1.8. In case of the Hall conductivity, the pinning strength dependence was also observed. The Hall conductivity after irradiation exhibited a clear deviation from that of the unirradiated crystal at low temperatures. These results are in a good agreement with the work by Wang et al. [16] in which pinning plays an important role.

1. Introduction

The mixed-state Hall effect of the high-temperature superconductors has remained one of the most unsolved problems in understanding of flux motion of type II superconductors. One of the most controversial phenomena has been a sign reversal of the Hall effect near the superconducting transition

temperature T_c as temperature or magnetic field is varied [1-13]. This sign reversal of the Hall effect has been observed in most of the high- T_c superconductors [1-12] as well as in some conventional superconductors [1,13]. Furthermore, a puzzling scaling behavior between the Hall resistivity ρ_{xy} and the longitudinal resistivity ρ_{xx} has been observed as $\rho_{xy} = A\rho_{xx}^\beta$ with the scaling exponent $\beta \sim 2$ in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (BSCCO) and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ (TBCCO) films [7,11], and $\beta \sim 1.7$ in $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) films [2].

A number of theoretical predictions have been proposed concerning the Hall effect in the mixed state. A phenomenological model resulting $\rho_{xy} = A\rho_{xx}^2$ in the thermally assisted flux-flow region has been put forward by Vinokur et al. [15], where the coefficient A was assumed to be pinning independent. Their results seem to be in agreement with scaling exponents of both weakly pinned systems of BSCCO single crystals ($\beta = 2.0 \pm 0.1$) [9] and rather strongly pinned systems of heavy-ion-irradiated TBCCO films ($\beta = 1.85 \pm 0.1$ and ~ 2.0) [7,11]. However, assuming that the coefficient A is a constant needs further microscopic justification [16].

Recently, Wang, Dong, and Ting [16] modified their earlier work [17] to develop a unified theory for the Hall effect including both the pinning effect and the thermal fluctuations. They [16] could rigorously explain the scaling behavior and the anomalous sign reversal of the Hall effect by especially taking into account the backflow current due to pinning. In this case the scaling exponent β then changes from 2 to 1.5 as the pinning strength increases, and the coefficient A is no longer pinning independent.

A decisive experiment that can test the role of pinning on the Hall effect is to measure the Hall conductivity, or resistivity in some cases, before and after heavy-ion irradiation since columnar defects formed along the heavy-ion tracks are very effective pinning centers [18]. The first attempt was made by Budhani et al. [11] on Ag-ion irradiated TBCCO films. They observed that the scaling behavior remains unaffected even after irradiation and the sign anomaly diminishes with increasing defect density. So they suggested that pinning is not responsible for the sign reversal. Later Samoilov et al. [17] measured the Hall conductivity of YBCO single crystals and TBCCO films before and after Pb-ion irradiation. Based on their finding, Samoilov et al. [7] argued that the pinning enhancement does not modify the behavior of the Hall conductivity, which we believe bears a slight problem in interpreting the data as will be discussed later.

In this proceeding we report the first and clear observation of the pinning-strength dependence of mixed state Hall effect in its scaling behavior and Hall conductivity of twinned YBCO single crystals with columnar defects.

2. Experimental

The single crystals of YBCO were grown by the standard flux technique. The crystals were cleaved by bar-shaped samples suitable for Hall effect measurements and were mounted on sapphire substrates. The crystals have typical dimensions of $1 \times 0.8 \times 0.03$ mm³. The electrical contacts (< 0.1 Ω) were made by Ag evaporation followed by annealing at 400 °C in O₂ atmosphere for 12 hours. The samples from the same batch were irradiated at 0 °C by 740-MeV Sn and Xe ions, which were produced by the Argonne Tandem Linear Accelerator System at the Argonne National Laboratory. The ion beam was aligned parallel to the *c* axis of the samples and a thin gold foil was inserted in the beam line to make sure a uniform beam profile over the sample width. The irradiation doses of 5×10^{10} , 1×10^{11} , and 1.5×10^{11} ions/cm² were chosen so that the matching fields B_4 , at which the density of columnar defects matches to the vortex density, correspond to ~ 1 , 2, and 3 T, respectively. YBCO crystals of 1 and 2 T dose are irradiated with Sn ions, whereas 3 T dose crystal is irradiated with Xe ions.

The Hall resistivity ρ_{xy} and longitudinal resistivity ρ_{xx} were measured by standard 5-probe dc method using the current source (Keithley 224) and the picovoltmeter (Keithley 2001 with 1801 preamp). The magnetic fields were applied parallel to the *c* axis of YBCO crystal, and ρ_{xy} was deduced from the antisymmetric part of Hall voltage under magnetic field reversal. The current density used for these measurements was ~ 20 A/cm². Twisted cryogenic coaxial cables are used for voltage leads to minimize the extrinsic noise pickup.

3. Results and Discussion

Typical resistive transitions of two crystals, $B_4 = 0$ (unirradiated, open symbols) and 2 T dose (solid symbols), are shown in Fig. 1 as a function of reduced temperature $t = T/T_c$ in magnetic fields of 2 and 4 T. Enhancement of the onset of ρ_{xx} in magnetic fields due to heavy-ion irradiation is clearly visible, in agreement with related works on samples containing columnar defects [7,11]. The figure is presented in reduced temperature t and reduced resistivity $r \equiv \rho_{xx}(T) / \rho_{xx}(T_c)$ in order to account for the difference of T_c and normal state resistivity [19]. Actual T_c 's used here were determined from the peak temperatures of dR/dT curves and they are 93.8 and 93.1 K, respectively, for $B_4 = 0$ and 2 T-dose crystals. At higher temperature where $r > 0.6$, longitudinal resistivity for both samples are closely

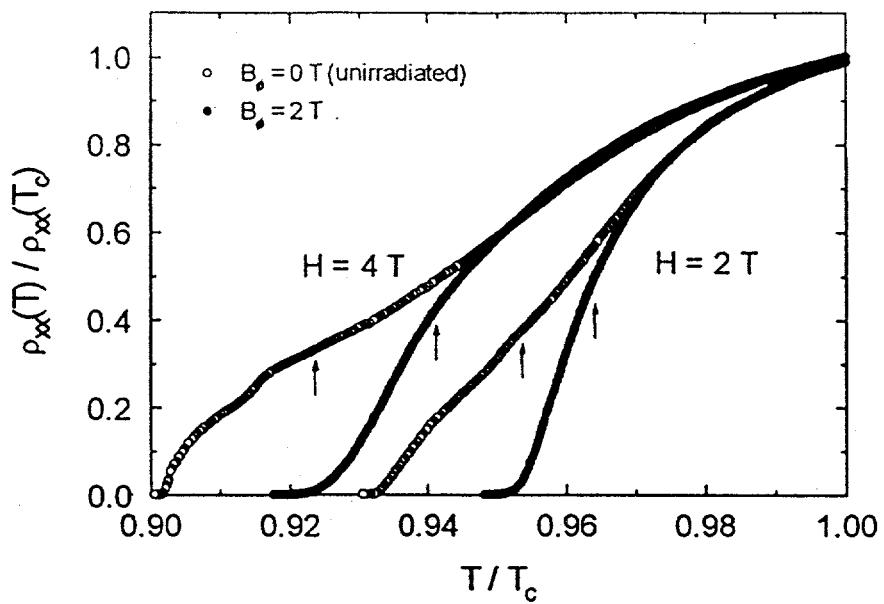


Fig. 1. Longitudinal resistivity of two twinned $\text{YBa}_2\text{Cu}_3\text{O}_7$ single crystals, $B_0 = 0$ (unirradiated, open symbols) and 2 T dose (solid symbols) shown as a function of reduced temperature $t = T/T_c$ in magnetic fields of 2 and 4 T. Arrows indicate the negative peak positions of the Hall resistivity shown in Fig. 2.

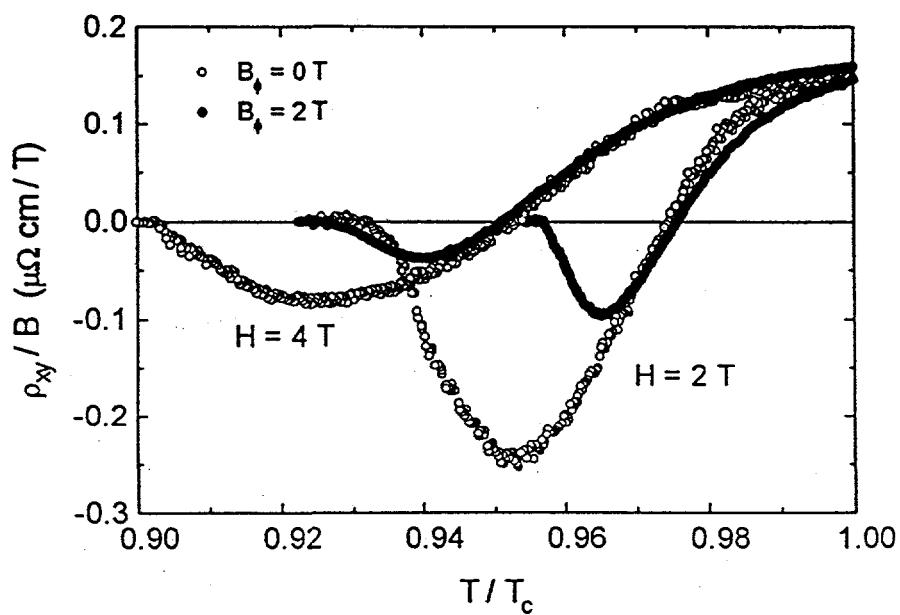


Fig. 2. Hall coefficient of two twinned $\text{YBa}_2\text{Cu}_3\text{O}_7$ single crystals, $B_0 = 0$ (unirradiated, open symbols) and 2 T dose (solid symbols).

together, but they begin to deviate for $r < 0.6$, showing the region of effective pinning due to columnar defects. Note that kink structure, known as the characteristics of twin-boundary pinning [20], near the foot of transition of the unirradiated sample is no longer observable in the irradiated one. Similar disappearance of kink in electron-irradiated YBCO crystal has been reported [19]. The other crystals with $B_d = 1$ and 3 T dose showed similar behavior.

The corresponding Hall coefficient ρ_{xy}/B are shown in Fig. 2. Sign reversal of the Hall effect was observed in both irradiated and unirradiated samples as temperature is lowered. Here again ρ_{xy}/B curves for both samples follow closely each other in the same temperature region of $r > 0.6$. The onset of ρ_{xy} as well as the negative peak positions shift to higher temperature after irradiation. The locations of negative peaks of ρ_{xy}/B are shown as arrows in Fig. 1. Relative upward shift of peak position in 2 T field along the $\rho_{xx}(T) / \rho_{xx}(T_c)$ curve is larger than that in 4 T field proving that vortex pinning for $B_d = 2$ T dose is more effective around 2 T field.

In Fig. 3, we show the scaling behavior between the Hall resistivity ρ_{xy} and longitudinal resistivity ρ_{xx} , $\rho_{xy} = A\rho_{xx}^\beta$, for crystals of $B_d = 0, 1, 2$, and 3 T dose for magnetic fields of 2 and 4 T. The scaling behavior holds in the temperature region below the negative peak of ρ_{xy} where pinning is effective, i.e., $r < 0.4$. The striking difference between the irradiated and unirradiated samples is their scaling exponent β . For irradiated crystals, $\beta = 1.55 \pm 0.1$ was observed for all fields, whereas for the unirradiated sample, $\beta = 1.8 \pm 0.1$ for $B = 2$ T increasing to 2.0 ± 0.1 in higher fields were observed.

According to Vinokur et al. [15], scaling behavior of the Hall resistivity in the mixed state of HTS is a general feature of any vortex state in the presence of the quenched disorder and thermal noises. Using the force balance equation for a stationary moving vortex, they showed that pinning just renormalize the drag force term, not affecting the Hall conductivity term. Their main results are that Hall conductivity σ_{xy} ($\approx \rho_{xy}/\rho_{xx}^2$) does not depend on disorder and the scaling exponent β is exactly 2, which can be summarized as

$$\rho_{xy} = \frac{\alpha \rho_{xx}^2}{\Phi_0 B} \quad (1)$$

where Φ_0 is the flux quantum, and α is a pinning independent parameter related to the Hall angle.

On the other hand, Wang et al. [16] recently developed a new theory for the flux motion for the mixed state Hall effect. They included both pinning-induced backflow and thermal fluctuations in the force balance equation. Then, an additional transverse term proportional to $\mathbf{F}_p \times \mathbf{n}$ with \mathbf{F}_p pinning force and \mathbf{n} a unit vector in the direction of magnetic field, induced due to the backflow current inside

the normal core, appears in the drag force. This transverse term is the main difference between two models. After time average on vortex velocity, the Hall scaling is given by

$$\rho_{xy} = \frac{\beta_0 \rho_{xx}^2}{\Phi_0 B} \{ \eta(1 - \bar{\gamma}) - 2\bar{\gamma}\Gamma(v_L) \} \quad (2)$$

where $\beta_0 = \mu_m H_{c2}$ with μ_m being the mobility of the charge carrier and H_{c2} being the upper critical field, η is the usual viscous coefficient, $\bar{\gamma} = \gamma(1 - \bar{H}/H_{c2})$ is proportional to γ , the parameter describing contact force on the surface of core with \bar{H} the average magnetic field over the core, and $\Gamma(v_L)$ is the coefficient of the time average of pinning force $\langle F_p \rangle = -\Gamma(v_L) v_L$. When $\gamma \sim 1$ in the region of relatively high temperatures, the negative Hall effect appears if pinning is not negligible.

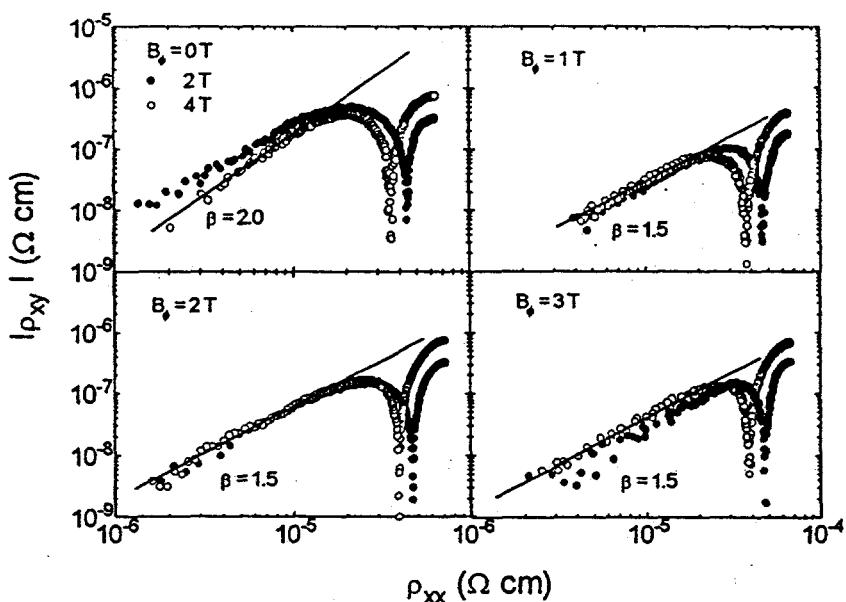


Fig. 3. Scaling behavior, $\rho_{xy} = A \rho_{xx}^\beta$, between the Hall resistivity ρ_{xy} and longitudinal resistivity ρ_{xx} of $\text{YBa}_2\text{Cu}_3\text{O}_7$ crystals with $B_4 = 0$ (top left), 1 (top right), 2 (bottom left), and 3 T dose (bottom right). For irradiated crystals, $\beta = 1.55 \pm 0.1$ was observed in all fields, whereas for the unirradiated sample, $\beta = 1.8 \pm 0.1$ for $B = 2$ T increasing to 2.0 ± 0.1 in higher fields were observed. Lines are fit to the power law dependence.

For the Hall scaling behavior, there are two distinct regimes according to Eq. 2. For systems with weak pinning, that is $\Gamma(v_L) \ll \eta \bar{H} / H_{c2}$, Eq. 2 becomes $\rho_{xy} \sim A \rho_{xx}^2$, resulting the same scaling exponent as Eq. 1. But in case of strong pinning, that is $\Gamma(v_L) \gg \eta \bar{H} / H_{c2}$, the scaling exponent β is

no longer 2. Since $\Gamma(v_L) \sim v_L^{-1/2}$ in the strong pinning case [21], scaling behavior modifies to $\rho_{xy} \sim A\rho_{xx}^{1.5}$. Between two limiting regimes, $1.5 < \beta < 2.0$ is expected [16].

Comparing both theory with our results in Fig. 3, we find that the model by Wang et al. [16] which explicitly includes the pinning-induced backflow effect is more appropriate for systems with columnar defects. As a matter of fact, $\beta = 1.55 \pm 0.1$ for the irradiated YBCO single crystals with $B_d = 1, 2$, and 3 T dose is very close to the theoretical estimation of 1.5. For unirradiated crystal, the result of $\beta = 1.8 \pm 0.1$ for $B = 2$ T increasing to 2.0 ± 0.1 in higher fields also agrees with the weak pinning case. These results are a strong indication of the pinning-strength dependence of mixed state Hall effect. Slight field dependence of β for unirradiated crystal too can be explained by this model. At lower fields, twin boundaries can be effective pinning centers so that β can be slightly smaller than the weak-pinning case, but at higher fields where the density of vortices sufficiently outnumbers the density of pinning centers, this case is much closer to the ideal weak-pinning case so that β becomes 2.

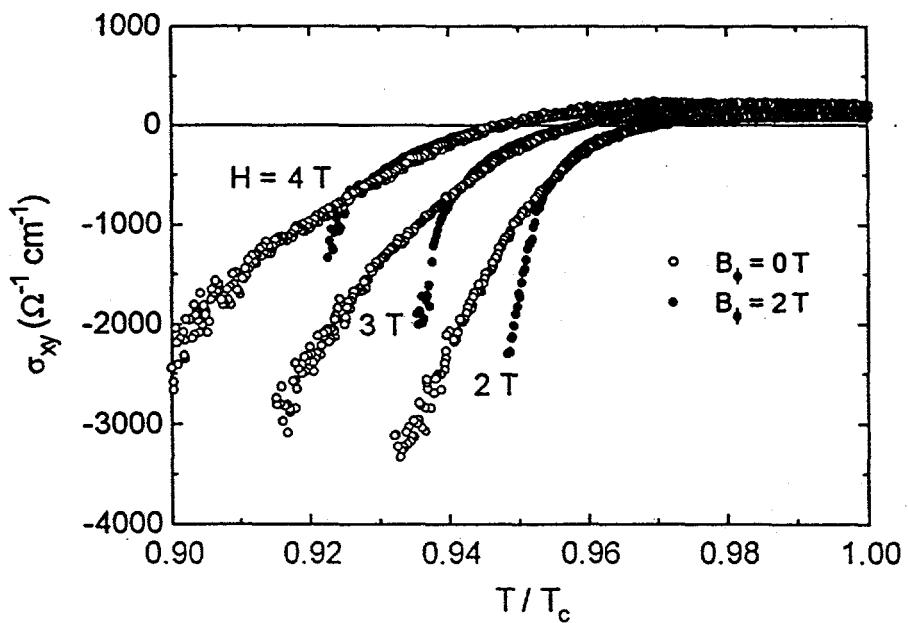


Fig. 4. Hall conductivity of $\text{YBa}_2\text{Cu}_3\text{O}_7$ crystals with $B_d = 0$ (open symbols) and 2 T dose (solid symbols) as a function of reduced temperature in magnetic fields of 2, 3, and 4 T. The Hall conductivity of $B_d = 2$ T shows a sharp deviation from the unirradiated one at low temperatures.

The fact that $\beta = 1.8 \pm 0.1$ at 2 T in the unirradiated crystals is not inconsistent with the earlier work by Luo et al. on YBCO films [2], where $\beta = 1.7 \pm 0.2$ was obtained for all fields above 1.4 T.

Only the difference is that films usually contains higher density of pinning sites than twinned crystals, thus β for films seems remain unchanged even in high fields. Wöltgens et al. measured nonlinear Hall resistivity in YBCO films near the vortex glass transition and showed that scaling behavior obeys $\rho_{xy} \sim A\rho_{xx}^{2.0 \pm 0.2}$ over a wide range of current densities [3]. However, in a small current regime that corresponds to the present window of the experiment, the data clearly show that the scaling exponent is less than 2.0, consistent with the results by Luo et al. [2] and our data.

Similar measurements on epitaxial TBCCO films containing columnar defects were made by Budhani et al. [11] and Samoilov et al. [7]. They both observed that the same scaling behavior persists even after irradiation. Since the vortex structure of TBCCO is believed to be two dimensional in the region where scaling law holds and thin films inherently contains higher defects, the pinning enhancement may not be as dramatic as the case of YBCO crystals. We note that no work has ever been reported on the scaling behavior of the Hall resistivity in YBCO samples after heavy-ion irradiation.

In the same work, Samoilov et al. [7] showed the Hall conductivity of YBCO single crystals before and after Pb-ion irradiation (Fig. 3 of Ref. 7). Since the Hall conductivity according to Vinokur et al. [15], is given as $\sigma_{xy} = \rho_{xy}/\rho_{xx}^2 = \alpha/(B\Phi_0)$, one can examine the validity of Eq. 1, i.e., independence of α on pinning, by plotting σ_{xy} before and after irradiation. In their plot, however, σ_{xy} is shown as a function of temperature, *not as a function of reduced temperature*. Although their data are very valid, the conclusion that σ_{xy} is unaffected by irradiation based on their plot seems misleading. We argue that in order to compare the physical properties of samples with different T_c , one should plot the data in the reduced temperature scale, not in the real temperature scale. Thus we plot the Hall conductivity of $B_0 = 0$ and 2 T dose as a function of reduced temperature in Fig. 4. The Hall conductivity of $B_0 = 2$ T follows that of the unirradiated one until it sharply deviates at low temperatures. This unambiguous drops at low temperatures is another evidence of the pinning-strength dependence of mixed state Hall effect. We point out that if the data by Samoilov et al. [7] were replotted as a function of reduced temperature after correcting T_c decrease of ~ 0.3 K after irradiation, their Fig. 3 in Ref. 7 will more look like our Fig. 4. In this view point our result is completely consistent with the result by Samoilov et al. [7]. The direction of deviation of σ_{xy} after irradiation is also consistent with Eq. 2. The presence of stronger pinning will make σ_{xy} more negative, which is exactly observed.

As a final note, Samoilov et al. also showed that σ_{xy} of TBCCO films does not change after irradiation [7]. In this case, T_c drop after irradiation is negligible compared to the broad

superconducting transition, so their conclusion that the Hall conductivity does not depend on the pinning strength remains valid only in case of TBCCO films. This result together with that of Ref. 11 seems to imply that effect of columnar defects on the Hall effect may not be observable in thin films presumably because of higher defect density even in unirradiated thin films.

4. Summary

We unambiguously showed that strong pinning induced by heavy-ion irradiation indeed modify the mixed state Hall effect in YBCO crystals. The Hall effect scaling exponent for the irradiated crystals was found to be $\beta = 1.55 \pm 0.1$, different from $\beta \geq 1.8$ for the unirradiated one. The Hall conductivity also changed after irradiation. These results are inconsistent with the model by Vinokur et al. in which pinning does not modify the Hall conductivity. Instead our result are in a good agreement with the recent theory including both the backflow effect due to pinning and thermal fluctuations in which β should decrease from 2.0 to 1.5 as the pinning strength increases.

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References

- [1]. S.J. Hagen, C.J. Lobb, R.L. Greene, M.G. Forrester, and J.H. Kang, Phys. Rev. **B41**, 11630 (1990).
- [2]. J. Luo, T.P. Orlando, J.M. Graybeal, X.D. Wu, and R. Muenchausen, Phys. Rev. Lett. **68**, 690 (1992).
- [3]. P.J.M. Wöltgens, C. Dekker, and H.W. de Wijn, Phys. Rev. Lett. **71**, 3858 (1993).
- [4]. J.P. Rice, N. Rigakis, D.M. Ginsberg, and J.M. Mochel, Phys. Rev. **B46**, 11050 (1992).

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- [5]. J.M. Harris, N.P. Ong, and Y.F. Yan, Phys. Rev. Lett. **71**, 1455 (1993).
- [6]. M.N. Kunchur, D.K. Christen, C.E. Klaubunde, and J.M. Phillips, Phys. Rev. Lett. **72**, 2259 (1994).
- [7]. A.V. Samoilov, A. Legris, F. Rullier-Albenque, P. Lejay, S. Bouffard, Z.G. Ivanov, L.-G. Johansson, Phys. Rev. Lett. **74**, 2351 (1995).
- [8]. Y.X. Jia, J.Z. Liu, M.D. Lan, and R.N. Shelton, Phys. Rev. **B47**, 6043 (1993).
- [9]. A.V. Samoilov, Phys. Rev. Lett. **71**, 617 (1993), and references therein.
- [10]. S.J. Hagen, C.J. Lobb, and R.L. Greene, and M. Eddy, Phys. Rev. **B43**, 6246 (1991).
- [11]. R.C. Budhani, S.H. Liou, and Z.X. Cai, Phys. Rev. Lett. **71**, 621 (1993).
- [12]. A.V. Samoilov, Z.G. Ivanov, L.-G. Johansson, Phys. Rev. **B49**, 3667 (1994).
- [13]. A.W. Smith, T.W. Clinton, C.C. Tsuei, and C.J. Lobb, Phys. Rev. **B49**, 12927 (1994).
- [14]. A.T. Dorsey and M.P.A. Fisher, Phys. Rev. Lett. **68**, 694 (1992).
- [15]. V.M. Vinokur, V.B. Geshkenbein, M.V. Feigel'man, and G. Blatter, Phys. Rev. Lett. **71**, 1242 (1993).
- [16]. Z.D. Wang, J. Dong, and C.S. Ting, Phys. Rev. Lett. **72**, 3875 (1994).
- [17]. Z.D. Wang and C.S. Ting, Phys. Rev. Lett. **67**, 3618 (1991); Phys. Rev. **B46**, 284 (1992).
- [18]. for example, L. Civale, A.D. Marwick, M.W. McElfresh, T.K. Worthington, M.A. Kirk, J.R. Thompson, L. Kirusin-Elbaum, Y. Sun, J.R. Clem, and F. Holtzberg, Phys. Rev. Lett. **67**, 648 (1991).
- [19]. J.A. Fendrich, W.K. Kwok, J. Giapintzakis, J. van der Beek, V.M. Vinokur, S. Fleshler, U. Welp, H.K. Viswanathan, and G.W. Crabtree, Phys. Rev. Lett. **74**, 1210 (1995).
- [20]. W.K. Kwok, J.A. Fendrich, C.J. van der Beek, and G.W. Crabtree, Phys. Rev. Lett. **73**, 2614 (1994).
- [21]. V.M. Vinokur, M.V. Feigel'man, V.B. Geshkenbein, and A.I. Larkin, Phys. Rev. Lett. **65**, 259 (1990).
- [22]. D.H. Kim, K.E. Gray, R.T. Kampwirth, J.C. Smith, D.S. Richardson, T.J. Marks, J.H. Kang, and J. Talvacchio, and M. Eddy, Physica **C177**, 431 (1991).