

## Upper-critical fields of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ epitaxial thin films with variable oxygen deficiency $\delta$

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Fluctuation analysis in the limit of high magnetic fields was performed on three epitaxial thin films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  for various oxygen deficiencies  $\delta < 0.3$ . On the 90-K plateau, the three-dimensional (3D) limit yielded an  $H_{c2}(T)$  slope of  $-1.7$  T/K for  $H \parallel c$ , consistent with previous observations of transport and magnetic properties. Moreover, the 3D scaling showed better convergence than the 2D scaling, which gave relatively low values of  $H_{c2}$ . In contrast, the transitions were not adequately described by either scaling for  $T_c$  off the 90-K plateau; it is speculated that this is due to an extrinsic broadening of the transitions, possibly due to the lack of a complete percolation path of the ortho- $I$  phase ( $\delta=0$ ).

### I. INTRODUCTION

Early work on oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  led to the discovery of the now well-known 90 and 60 K  $T_c$  vs  $\delta$  plateaus.<sup>1</sup> Although the origin of these features has proved difficult to elucidate, several elaborate electronic models<sup>2-4</sup> and phase-separation scenarios<sup>5-7</sup> have been proposed. In our previous work on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  epitaxial thin films, the critical current density  $J_c$  was observed to extrapolate toward zero as the oxygen deficiency  $\delta$  neared the edge of the 90-K  $T_c$  plateau, while the flux-creep activation energy remained constant.<sup>7</sup> This finding suggests that the 90-K  $T_c$  plateau occurs as a result of a complete percolation path of the fully oxygenated ortho- $I$   $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase.<sup>8,9</sup> In contrast, Ossandon *et al.* showed that an increasing coherence volume  $\xi^3$  with  $\delta$  could lead to a relatively constant flux-creep activation energy  $U_0 = (H_c^2/8\pi)\xi_{ab}^2 \xi_c$  on the 90-K plateau by allowing the increasing coherence volume to counteract the decreasing condensation energy  $H_c^2/8\pi$ .<sup>10</sup> In this model, the decreasing critical current density  $J_c(\delta)$  simply reflects a decreasing  $J_{c0} \propto (H_c^2/8\pi)\xi_{ab}$  which is the critical current density in the absence of flux creep.<sup>10</sup> If an electronic mechanism is responsible for the 90-K  $T_c$  plateau, the coherence length  $\xi$  must increase with oxygen deficiency in order to explain the constant pinning activation energy which is observed on this plateau. Therefore,

to better understand the true origin of these  $T_c(\delta)$  plateaus and to provide clues as to the possible pairing mechanism, we examined systematic changes in the fluctuation conductivity  $\sigma_f(T, H)$  and the transition temperature  $T_c$  as a function of oxygen deficiency  $\delta$ . The high-field fluctuations<sup>11-13</sup> are generally accepted as a means of determining the upper-critical field  $H_{c2}$ . If the fluctuations yield an  $H_{c2}$  plateau coinciding with the 90-K plateau, this finding would support the phase separation-percolation scenario for the  $T_c$  vs  $\delta$  plateaus. On the other hand, if  $H_{c2}$  decreases with  $\delta$ , electronic mechanisms would remain a viable explanation for the  $T_c$  vs  $\delta$  plateaus. Therefore, these important measurements were performed on three high-quality epitaxial thin films that were rendered oxygen deficient by thermal processing under carefully controlled conditions.<sup>14</sup>

Other issues also motivated the present fluctuation study. First, most high-field fluctuation theories neglect the Maki-Thompson processes<sup>15</sup> which are assumed to be negligible at very high fields. Comparison of the upper-critical fields  $H_{c2}$  determined by the present high-field fluctuation analysis to those determined by applying other techniques, such as the Hao *et al.* analysis<sup>16</sup> to the reversible diamagnetism curves, may help to decide whether or not these processes are, indeed, negligible in the high-field regime. Second, the fluctuation analysis may provide the only means of estimating  $H_{c2}$  in some materi-

als such as extremely thin films, e.g., superlattices. Again, comparing these fluctuation-derived  $H_{c2}$  values to those determined by other techniques may provide clues as to whether or not the fluctuation analysis provides reliable upper-critical fields.

Experimentally, we found that while on the 90-K  $T_c$  plateau, the fluctuation analysis yielded an  $H_{c2}(\delta)$  plateau with a slope of  $dH_{c2}/dT|_{T_c} \approx -1.7 \text{ T/K}$  for  $H||c$ . On the contrary, the transitions obtained off the 90-K plateau ( $\delta > 0.2$ ) were not accurately described by the fluctuation theory; this feature will be attributed to an extrinsic broadening of the transitions. We argue that this may result from the loss of a percolation path of fully oxygenated ortho- $I$  phase. Finally, to support this speculation, independent data will be presented to support the coexistence of multiple phases in oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

Studies of fluctuation effects in superconductors have recently been revived due to the discovery of the high- $T_c$  materials. In this work, we utilize the recent in-field fluctuation theories<sup>11,12</sup> (the derivations of Ullah and Dorsey are particularly useful) to deduce the  $H_{c2}$  slopes for  $H||c$ . The fluctuation theories were developed in the framework of the Lawrence-Doniach model,<sup>17</sup> which accounts for the layered structure of the high- $T_c$  materials. The theory of Ullah and Dorsey<sup>11</sup> gives the following set of equations for the fluctuation conductivities with either three-dimensional (3D) or 2D scaling:

$$\left(\frac{H}{T}\right)^{1/2} \sigma_{yy}^{2D} = g \left[ A \frac{T - T_c(H)}{(TH)^{1/2}} \right], \quad (1)$$

$$\left(\frac{H^{1/3}}{T^{2/3}}\right) \sigma_{yy}^{3D} = g \left[ A \frac{T - T_c(H)}{(TH)^{2/3}} \right], \quad (2)$$

$$(TH)^{1/2} \sigma_{zz}^{2D} = f \left[ A \frac{T - T_c(H)}{(TH)^{1/2}} \right]^3, \quad (3)$$

$$\sigma_{zz}^{3D} = f \left[ A \frac{T - T_c(H)}{(TH)^{2/3}} \right]^3. \quad (4)$$

In these equations,  $\sigma_{ii}$  is the fluctuation conductivity along the  $i$ th crystal axis (i.e.,  $\sigma_{yy}$  denotes  $||ab$  plane while  $\sigma_{zz}$  denotes  $\perp ab$  plane),  $H = H_z$  is the applied magnetic field along the  $c$  axis, and  $T_c(H)$  is the mean-field transition temperature, which is field dependent. The unknown scaling functions  $g$  and  $f$  should be the same for all fields, and the constant  $A$  is independent of the temperature and field (the exact expression for  $A$  is unimportant here, but is described in detail by Han *et al.*<sup>18</sup>). The only adjustable parameter is  $T_c(H)$ . Its values are selected by simply plotting the argument of each side of the equation of interest, while selecting  $T_c(H)$  such that the transitions for each magnetic field fall on a universal curve. Interestingly, the best choices of  $T_c(H)$  usually correspond to a linear  $H_{c2}$  vs  $T$  dependence near  $T_c$ . Equations (1) and (2) apply to the  $c$ -oriented epitaxial films used in this study, whereas Eqs. (3) and (4) could be applied to any basal-plane-oriented film, for example.

## II. EXPERIMENTAL ASPECTS

The three highly crystalline [verified by 2% ion-channeling Rutherford backscattering spectroscopy (RBS) yields] epitaxial thin films included in this study were grown by the  $\text{BaF}_2$  process.<sup>19</sup> For electrical transport measurements, the films were photolithographically patterned with a 3 mm long by a 50  $\mu\text{m}$  wide bridge. Gold dots were then sputtered onto contact areas to allow measurements of the resistivity  $\rho$  and transition temperature  $T_c$ , using standard dc techniques. Currents were systematically reversed to cancel thermal emfs. Contact resistances were less than 0.1 m $\Omega$  after the first full oxygenation anneal at 550°C in 1 atm  $\text{O}_2$ . This allowed easy, solder-free mounting and demounting with the use of Au-In-Au pressure pads and spring loaded contacts. Control of the oxygen deficiency  $\delta$  was provided by isobaric sequential anneals<sup>14</sup> at 550°C under reduced partial pressures of  $\text{O}_2$ . Thus, small changes in  $\rho$  and  $T_c$  as a function of  $\delta$  could be obtained in a given sample of fixed-bridge geometry, thereby eliminating the relative errors due to cross sectional differences. The effects of oxygen depletion were reversible, as demonstrated by a final anneal at 1 atm  $\text{O}_2$  that reestablished the starting properties of the films, even after 11 sequential anneals. Magnetic fields were applied parallel to the  $c$  axis as assumed in the fluctuation theory. From previous x-ray-diffraction studies<sup>7</sup> of four epitaxial thin films, we obtained a universal correlation between the relative change in the  $c$ -axis lattice parameter  $c$  and the normal-state conductivity  $\sigma$  for oxygen contents in the regime of the 90-K plateau ( $\delta < 0.2$ ). These correlations were combined with the average  $c$ -lattice expansions found by Cava *et al.*<sup>20</sup> and Jorgensen *et al.*<sup>21</sup> as a function of oxygen deficiency  $\delta$  to obtain the general relationship (valid for  $\delta < 0.3$ ),

$$\delta \approx 0.45 \left| \frac{\Delta\sigma}{\sigma_0} \right|. \quad (5)$$

Values of  $\delta$  can be obtained from Eq. (5), but must be regarded as provisional, since extrinsic factors such as substrate-induced strains may alter both the magnitude of the  $c$ -lattice parameter, as well as its response to  $\delta$ . It turns out that the exact value of the oxygen deficiency  $\delta$  is not critical since an apparent plateau in  $H_{c2}$  vs  $\delta$  was observed. Approximate values of  $\delta$  are only necessary to allow comparisons of the  $H_{c2}(\delta)$  values in this work to those obtained in bulk  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  utilizing magnetization measurement.<sup>22,23</sup>

## III. EXPERIMENTAL RESULTS

To minimize the impact of extrinsic transition broadening (e.g., broadening due to defects and/or inhomogeneity) on our fluctuation analysis, only the highest crystal quality, lowest defect-pinning films<sup>19</sup> were included in this fluctuation study. Figure 1 shows that the zero-field transition widths are on the order of  $\sim 0.5$ – $0.8$  K. In addition, the transition widths were not observed to broaden with oxygen deficiency  $\delta$  while on the 90-K plateau. Although there is no guarantee that inhom-

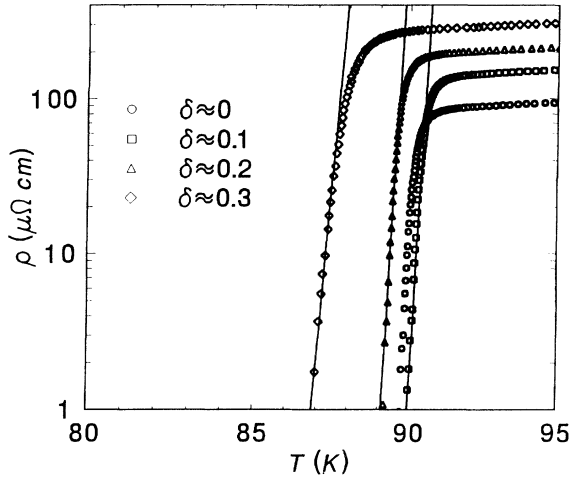


FIG. 1. Resistive transitions shown on a log-log plot. This graph indicates that the high-quality coevaporated films chosen for this fluctuation analysis have zero-field transition widths on the order of  $\sim 0.5$ – $0.8$  K. Moreover, the parallel shifts of the transitions occurring on the 90-K plateau ( $\delta \leq 0.2$ ) indicate that no additional broadening occurs with increasing oxygen deficiency  $\delta$ . In contrast, a slight broadening in the transitions does occur off the 90-K plateau ( $\delta \approx 0.3$ ).

generality does not adversely effect the in-field fluctuation analysis, if such extrinsic effects are indeed significant, we would probably expect to obtain an  $H_{c2}$  value that seriously disagrees with those reported using completely different techniques to obtain  $H_{c2}$ .

In the following discussion, we will see that application of the fluctuation theory to the experimental data on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  suggests the existence of an  $H_{c2}(\delta)$  plateau over the oxygen range  $6.8 \leq 7 - \delta \leq 7.0$  with a slope of  $dH_{c2}/dT|_{T_c} \approx -1.7$  T/K. This oxygen range corresponds to the complete range of the 90-K plateau in all three films. In Figs. 2(a)–2(d), the determination of the  $H_{c2}(T)$  slope near  $T_c$  is depicted by a two-step process that utilizes Eq. (2). In order to obtain  $dH_{c2}/dT$ , we first determine the fluctuation conductivity  $\sigma_f (= \sigma_{ii}^{3D,2D})$  by extrapolating the normal-state resistivity into the superconducting regime and then applying the relation

$$\sigma_f = \sigma_{\text{total}} - \frac{1}{\rho_0 + mT}. \quad (6)$$

Here  $\sigma_f$  is the fluctuation conductivity,  $\sigma_{\text{total}}$  is the observed conductivity,  $\rho_0$  and  $m$  are the constants describing the linear extrapolation of the normal-state resistivity

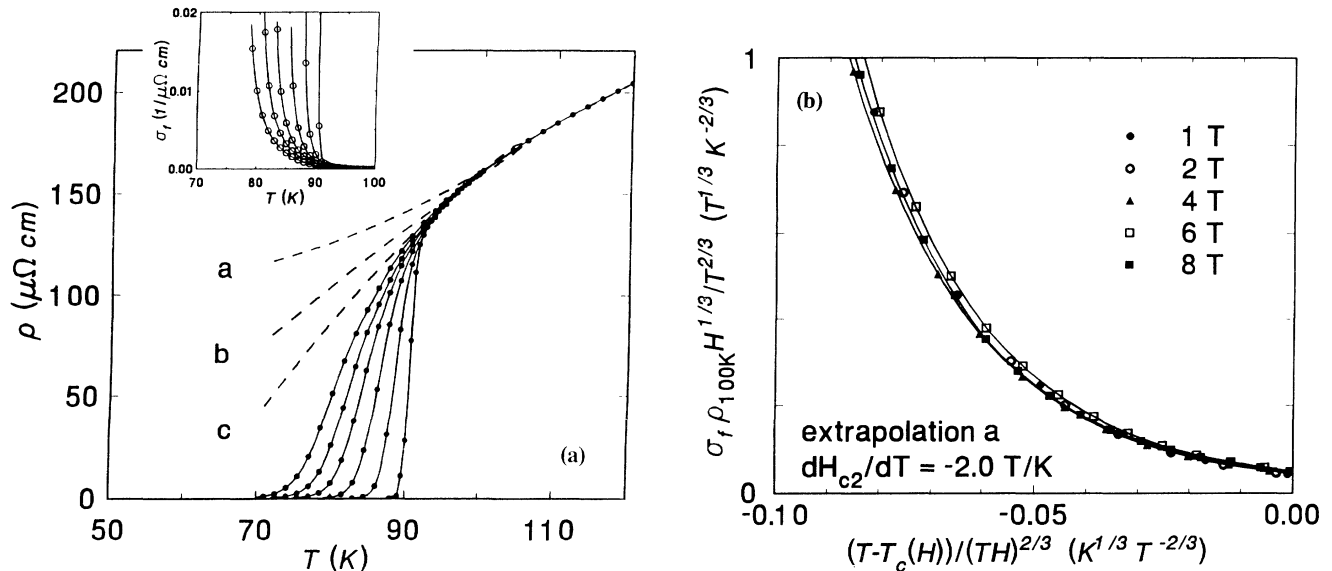


FIG. 2. Step-by-step determination of  $-dH_{c2}/dT$  by utilization of the high-field fluctuation theory. (a) First, the fluctuation conductivity  $\sigma_f$  (inset) is determined for various normal-state resistive extrapolations (dashed curves a, b, and c) as a function of temperature and applied field. (b–d) These are plotted according to Eq. (2) for each normal-state extrapolation on the 90-K plateau. The only adjustable parameters are the mean-field transition temperatures  $T_c(H)$ , which give  $T_c$  as a function of  $H_{c2}$ , and these are chosen in such a way as to generate the best universal curves shown. Since each extrapolation generated similar  $H_{c2}$  slopes, e.g.,  $(-1.7 \pm 0.3)$  T/K, the derived  $H_{c2}$  values appear to be more sensitive to the divergence of the in-field resistive transitions rather than on the chosen normal-state extrapolations. Therefore, all preceding derivations of  $H_{c2}$  will simply assume a linear resistive extrapolation. (e) Note that the transitions obtained off the 90-K  $T_c$  plateau are not adequately described by the fluctuation theory. (f) Moreover, the fluctuation conductivities plotted according to Eq. (1) indicates that the 2D scaling does not adequately describe the resistive fluctuations. The resistivity factor,  $\rho_{100K}$ , in the y values allows relative comparisons of the quality of fit to be made in each case.

into the superconducting state. Although linear extrapolations appear to be reasonable, it is not clear that these assumed extrapolations are the best choices. As a test, several extrapolations were tried [dashed curves labeled a, b, and c in Fig. 2(a)] and were found to generate remarkably similar  $H_{c2}$  slopes, i.e.,  $-2.0$ ,  $-1.7$ , and  $-1.4$  T/K, respectively, near  $T_c$ . Figures 2(b)–2(d) indicate that the fluctuation conductivities determined from each extrapolation are well described by the fluctuation theory. Since these resistive extrapolations were sufficiently different, this implied that the fluctuation analysis was not very sensitive to the exact choice of the extrapolation. Therefore, the derived  $H_{c2}$  values in this work simply assumed the linear extrapolation of the normal-state resistivity into the mixed state. Error bars on the  $H_{c2}$  slopes, although difficult to know with certainty, are believed to be no more than  $\pm 0.1$  T/K.

In order to determine the upper-critical field, the derived fluctuation conductivities  $\sigma_f$  were plotted in re-

duced form as shown in Figs. 2(b)–2(d), for example. The resulting  $H_{c2}$  curves were then obtained by choosing  $T_c(H)$  for each applied field in order to obtain a universal curve. For oxygen contents in the regime of the 90-K plateau, the 3D scaling [Eq. (2)] always gave the best convergence, assuming a linear  $H_{c2}$  vs  $T$  with a slope of  $-1.7$  T/K near  $T_c$ . Interestingly, the temperature dependence of  $H_{c2}$  in all three films extrapolated to zero at the midpoint of the self-field resistive transitions. Off the 90-K plateau, however, neither the 3D nor the 2D scaling accurately described the fluctuation regime of the in-field resistive transitions. For instance, the best fit possible for an oxygen content of  $7-\delta \approx 6.7$  was obtained by application of the 3D scaling and choosing an “enhanced”  $H_{c2}$  slope of about  $-2$  T/K. These resulting curves [Fig. 2(e)] clearly show differences in curvature at each applied field. Furthermore, the convergence of these curves progressively worsened as the oxygen content was sequentially reduced. As already stated, the 2D

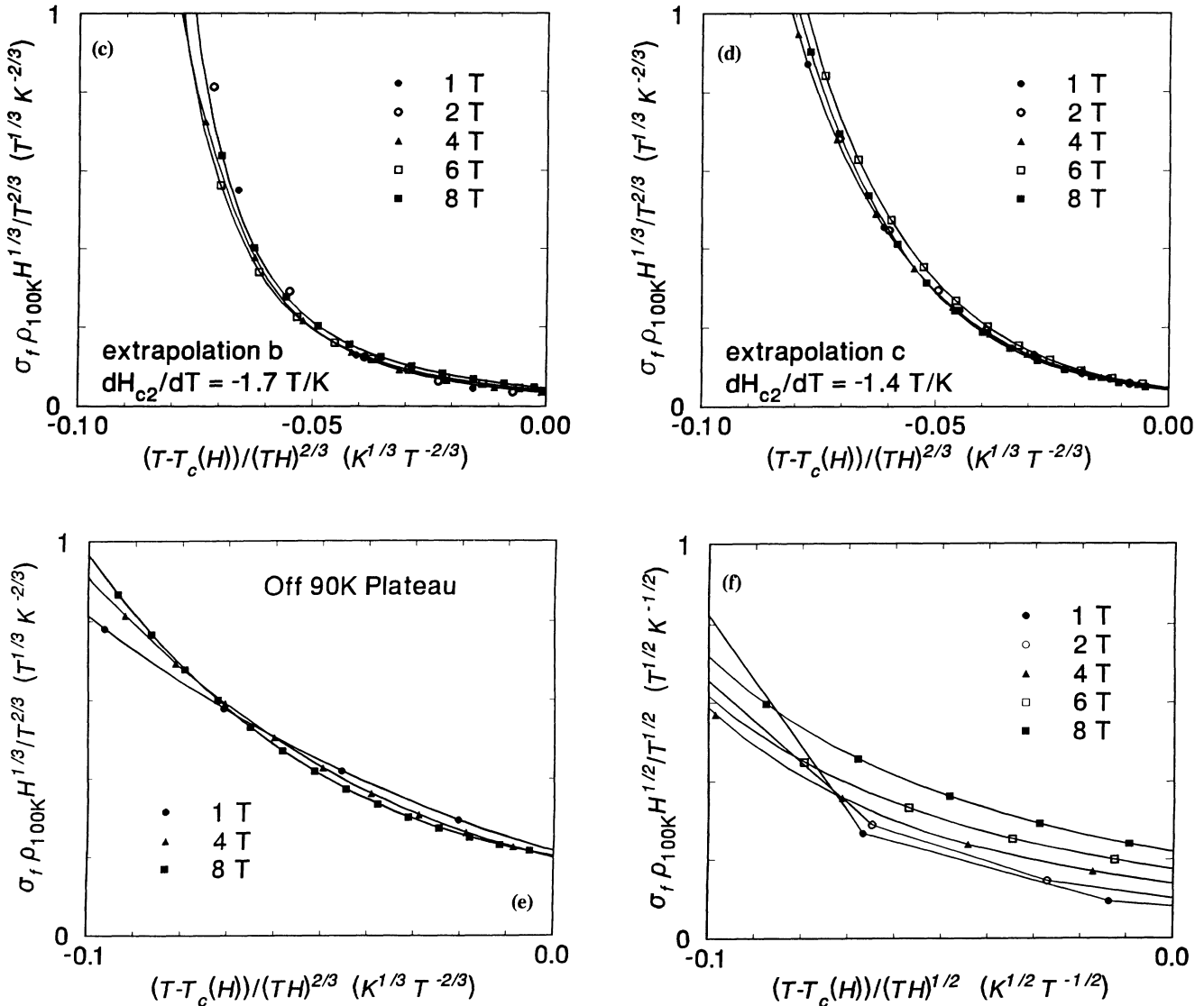


FIG. 2. (Continued).

scaling did not accurately describe the fluctuations at any oxygen content as depicted at full oxygenation in Fig. 2(f). This observation was previously reported in the fluctuation diamagnetism of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  crystals.<sup>24</sup> In addition, the 2D scaling also suggested lower  $H_{c2}$  slopes, e.g.,  $-1.2$  T/K near  $T_c$ .

The  $H_{c2}$  slopes determined by three different techniques are summarized in Fig. 3. This figure compares the present electrical transport fluctuation results to the equilibrium mixed-state magnetization analysis of Ossandon *et al.*<sup>22</sup> In the magnetization studies, application of the simple Ginzburg-Landau extrapolation (Welp *et al.*<sup>25</sup>) produced an initial  $H_{c2}(\delta)$  plateau of about  $-2.1$  T/K. Upon application of the more rigorous theory of Hao *et al.*,<sup>16</sup> the same data yielded a similar plateau, but with a smaller  $H_{c2}$  slope of  $-1.8$  T/K. Interestingly, the Hao *et al.* analysis for  $H_{c2}$  agrees reasonably well with the fluctuation analysis over the range of the observed 90-K plateau. More specifically, the magnetization studies yielded a 90-K plateau that spanned a smaller range of  $\delta$ , e.g.,  $\sim 6.89-7.00$ . In sum, these observations suggest that an  $H_{c2}(\delta)$  plateau is associated with the 90-K  $T_c$  plateau making an electronic mechanism an unlikely explanation for the coexisting 90 K  $T_c$  and pinning activation-energy plateaus.

For oxygen compositions occurring off the 90-K plateau (typically  $\delta \geq 0.2$ ), the resistive transitions taken in self-field for most  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples are broadened.<sup>7</sup> Figure 4(a) shows typical Hall transitions for compositions taken off the 90-K plateau which suggests a  $T_c$  distribution. Although uncommonly observed in the resistive transitions of oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , this apparent  $T_c$  distribution sometimes appears in the resistive transitions obtained off the 90-K plateau [Fig. 4(b)].<sup>26</sup> These data suggest that a discrete distribution of finely

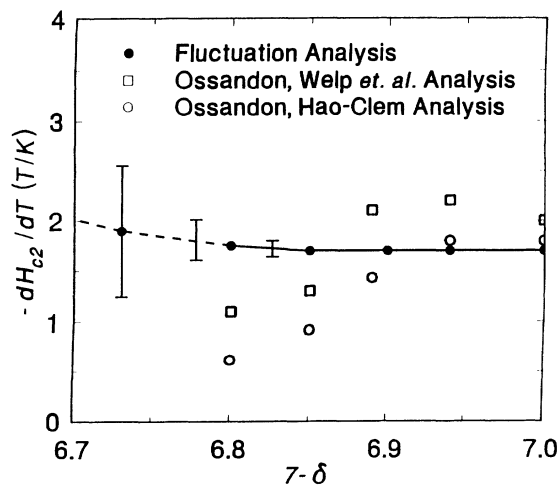


FIG. 3. Summary of the  $H_{c2}(T)$  slopes as a function of oxygen deficiency  $\delta$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  determined by the in-field fluctuation analysis of epitaxial thin films (filled circles). These are compared to the magnetization results of bulk, aligned  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  adapted from Ossandon *et al.*<sup>36</sup> (open symbols). The dashed curve indicates the failure of the fluctuation analysis to produce an adequate universal curve off the 90-K plateau.

dispersed  $T_c$ 's may exist in all oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples, in addition to the more prominent coexisting ortho-I, ortho-II, and tetragonal phases.<sup>8,9</sup> Moreover, previously published data of the field dependence of  $J_c$  indicated a granularlike critical current density at reduced oxygen contents, i.e., in the range  $\delta \geq 0.3$ .<sup>7</sup> Finally, the existence of coexisting phases in these high-quality epitaxial thin films prompted the following discussion concerning the effects of phase separation on the in-field fluctuation analysis.

#### IV. PHASE-SEPARATION EFFECTS

Considerable experimental evidence currently exists that supports a phase-separation phenomenon, i.e., chain-site oxygen clustering in oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .<sup>5-9,27,28</sup> Furthermore, such occurrences of phase separation may be directly responsible for both the 90- and 60-K plateaus observed in  $T_c$  vs  $\delta$ , via geometrical effects and the percolation of current.<sup>8</sup> Therefore, it was deemed necessary to determine the effects of phase separation on the "apparent"  $H_{c2}$  values, as determined from the above fluctuation theory. As a simple model, we assumed that oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  simply separated into regions of 90 and 85 K phases. Two sets of in-field resistive transitions were experimentally obtained—one at full oxygenation ( $T_c = 90$  K) and the other just off the 90-K plateau ( $T_c = 85$  K). The former set had an apparent  $dH_{c2}/dT|_{T_c} \approx -1.7$  T/K while the latter had an apparent  $dH_{c2}/dT|_{T_c} \approx -2.0$  T/K. Both parallel and series combinations of these two sets of resistive transitions were calculated as a function of temperature using  $R = R_{90\text{ K}} + R_{85\text{ K}}$  for the series combinations and  $1/R = 1/R_{90\text{ K}} + 1/R_{85\text{ K}}$  for the parallel combinations. The resulting resistive transitions were then analyzed in the framework of the fluctuation theory utilizing the 3D scaling. The resulting apparent values of  $-dH_{c2}/dT$  are shown as a function of the volume percentage of the 90-K phase in Fig. 5. These results indicate that the fluctuation analysis is sensitive only to the presence of the more conductive 90-K phase in a parallel conduction system. This important result indicates that geometrical errors should not lead to errors in the  $H_{c2}$  values as determined from the fluctuation analysis. In contrast, series combinations of these phases generate enormous false increases in  $-dH_{c2}/dT$ . For instance, a mere 0.3% of the 85-K phase in series with the 90-K phase leads to some error in the determined  $H_{c2}$ , even though such series combinations would have little effect on the overall resistivity [see Fig. 5 (inset)]. In this simulation, if the 85-K phase exceeded  $\sim 2\%$  of the total volume fraction, the fluctuation theory described the resistive transitions poorly; such results are similar to the actual experimental results taken off the 90-K plateau [Figs. 2(e) and 3]. In accordance with this model, the constant  $H_{c2}$  slopes of  $-1.7$  T/K observed across the 90-K plateau are believed to simply result from a complete percolation path of the fully oxygenated ortho-I  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase, while the failure of the fluctuation theory and broadening of the resistive transitions taken

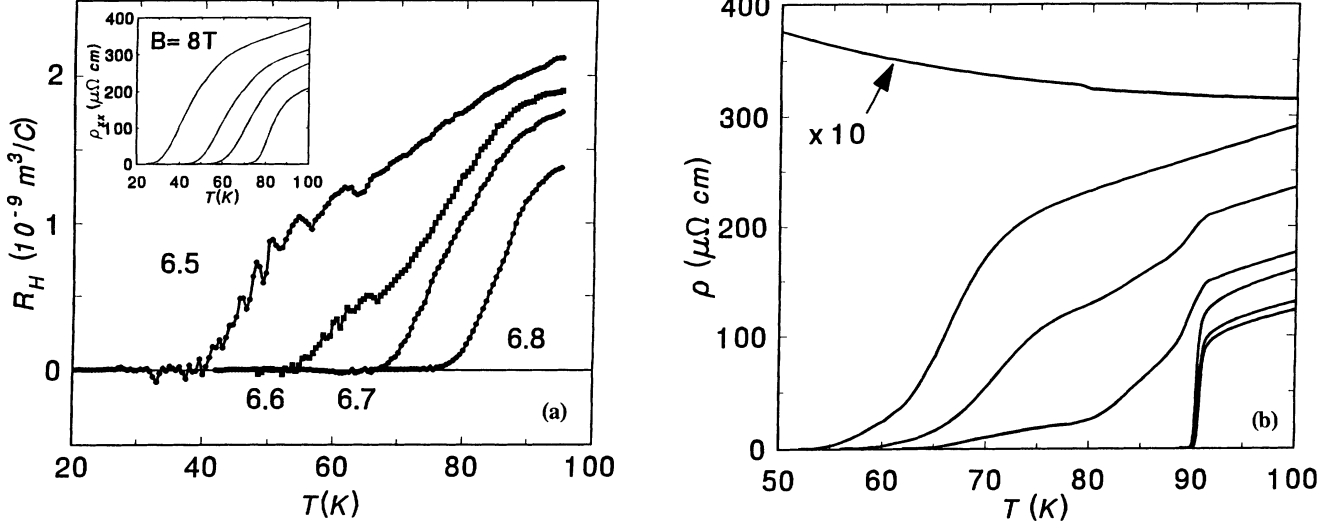


FIG. 4. Evidence for the coexistence of multiple phases at reduced oxygen contents in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . (a) Systematic “peaks” were observed in the Hall transitions of all samples whenever  $\delta \geq 0.3$ . These peaks suggest a  $T_c$  distribution that normally does not appear in the resistive transitions (typical transitions shown in the inset). (b) However, occasional resistive transitions at reduced oxygen contents are encountered which hint of these same coexisting phases. Note that the upper curve was obtained after annealing this sample at  $550^\circ\text{C}$  for 1 h in argon. The lack of any superconducting onsets argues against these transitions being due to an oxygen diffusion barrier. Obviously, these atypical samples cannot be used in the fluctuation analysis.

off the 90-K plateau seem to reflect the presence of a series, discrete  $T_c$  distribution.

### V. IMPLICATIONS FOR BCS THEORY

Unfortunately, universal results for  $H_{c2}(H||c)$  at all oxygen deficiencies  $\delta$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  cannot be deduced from the various experimental determinations of  $H_{c2}$  summarized in Fig. 3. Furthermore, the nonlinear  $T_c$  vs  $\delta$  behavior observed in oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  materials apparently occurs as a result of inhomogeneous oxygen doping. Nonetheless, the importance of knowing  $H_{c2}$  as a function of  $\delta$  will be stressed in the framework of simple BCS relationships, since quenching procedures might be utilized to produce more homogeneous thin films in future experiments. In the clean limit, if  $H_{c2}$  changes with  $\delta$  on the 90-K plateau due to electronic effects, then changes must occur in the Fermi velocity. Clean-limit BCS theory provides that

$$H_{c2}(0) = \frac{\Phi_0 \pi \Delta^2(0)}{2 \hbar^2 v_F^2} . \quad (7)$$

Moreover, recent measurements of the energy gap<sup>29</sup> give the strong-coupling result that

$$\Delta(0) = \frac{(6-8)}{2} k T_c . \quad (8)$$

In the above equations,  $\Phi_0$  is the flux quantum  $2.07 \times 10^{-7} \text{ G/cm}^2$ ,  $\Delta(0)$  is the superconducting energy

gap at the Fermi surface at absolute zero,  $v_F$  is the Fermi velocity of the superconducting charge carriers, and  $T_c$  is the superconducting transition temperature. Combining Eqs. (7) and (8) leads to the simple proportionality,

$$H_{c2}(0) \propto \frac{T_c^2}{v_F^2} . \quad (9)$$

Superconductivity is generally believed to be associated with the  $\text{CuO}_2$  planes, and from band-structure calculations, Yu *et al.*<sup>30</sup> have shown that the plane-related pieces of the Fermi surface are virtually identical between the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  phases. This suggests that the Fermi velocity is relatively insensitive to changes in the oxygen deficiency  $\delta$ . Thus, one might expect plateaulike behavior in the upper-critical field  $H_{c2}$  to be associated with the 90-K  $T_c$  vs  $\delta$  plateau. Unfortunately, Allen *et al.* give  $\langle v_{x,y}^2 \rangle^{1/2} = 2.3 \times 10^7 \text{ cm/s}$  based on band-structure calculations,<sup>31</sup> which implies  $H_{c2} \approx 35 \text{ kOe}$ , over one order of magnitude below the accepted value of  $H_{c2}$ .<sup>32</sup> This discrepancy may be resolved by either an uncertainty in the prefactor of Eq. (8) or by a non-BCS-type pairing mechanism that determines  $T_c$ . Recent evidence suggests that the maximum transition temperature of 92 K in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  may be due to a phase instability,<sup>33</sup> which could explain this  $H_{c2}$  discrepancy in addition to the enhanced values for the prefactors in Eq. (8) as observed by others.<sup>34</sup> Thus, we have shown that one might expect an  $H_{c2}$  plateau as a function of oxygen deficiency  $\delta$ , assuming BCS theory is applicable to the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system and that the 90-K plateau results from an electronic mechanism.

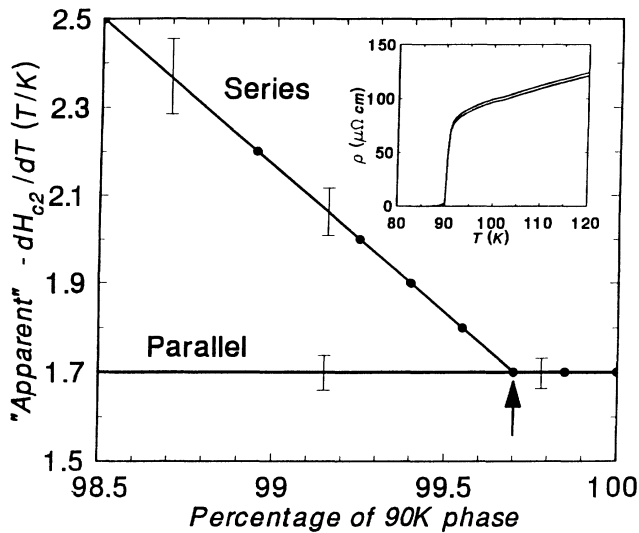


FIG. 5. Predicted effect of phase separation on the apparent  $H_{c2}$  slopes as derived from the fluctuation analysis. The model used to generate these results assumed that phase separation occurs between discrete regions of  $T_c = 90$  and  $85$  K. This simulation reveals that parallel conduction channels of similar phases should have no effect on the apparent  $H_{c2}$  values, whereas coexisting series phases should lead to significant increases in the apparent  $H_{c2}$  values above a certain threshold amount of the minority phase (arrow). The inset shows the resulting self-field resistive transitions for the following series phase cases: (top) 98.5% 90-K phase and (bottom) 100% 90-K phase.

## VI. SUMMARY

The fluctuation theory,<sup>11,12</sup> in the high-field limit, was applied to the in-field resistive transitions obtained from three high-quality epitaxial thin films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  at various oxygen deficiencies  $\delta$ . In each sample, an  $H_{c2}(\delta)$  plateau with a corresponding high-temperature slope of  $-1.7$  T/K was deduced for oxygen compositions occurring on the 90-K plateau, i.e., in the range  $6.8 \leq 7 - \delta \leq 7.0$ . In contrast, the in-field resistive transitions taken off the 90-K plateau, i.e.,  $\delta \geq 0.2$ , were not adequately described by the fluctuation theory, which may indicate the presence of coexisting series phases. Indeed, evidence for a discrete  $T_c$  distribution is observed in the Hall transitions and the field dependence of

$J_c/J_c(H=0)$  in oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . From this work, we speculate that the apparent  $H_{c2}$  plateaus simply reflect the existence of a percolation path of the more conductive, fully oxygenated ortho-I  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase in slightly oxygen deficient samples, since it was established that geometrical cross sectional errors do not change the apparent  $H_{c2}$  values as determined by this fluctuation analysis. This phase-separation scenario is also consistent with the observation of a constant flux-creep activation energy observed across the 90-K plateau in our previous work.<sup>7</sup> In addition, we established that the fluctuation analysis should lead to false increases of the apparent  $H_{c2}$  values whenever slightly different phases occur in series. This finding suggests that the high-field fluctuation analysis is probably an unreliable means of determining the upper-critical field except for the very best homogeneous superconductors. Unfortunately, the necessary degree of homogeneity required for these analyses probably occurs very infrequently in the high- $T_c$  superconductors due to their short coherence lengths  $\xi$ . However, since the derived upper-critical field at full oxygenation (oxygen clustering effects should be minimal near  $\delta \approx 0$ ) agrees with the upper-critical field determined by other techniques,<sup>10</sup> the high-field fluctuation theory appears to be a viable means of determining reasonable  $H_{c2}$  values. In addition, these agreements ( $\delta \approx 0$ ) also suggest that the Maki-Thompson processes<sup>15</sup> are negligible in the high-field regime. Finally, Däumling, Levine, and Shaw<sup>35</sup> have shown that the  $T_c$  vs  $\delta$  plateaus are absent in polycrystalline samples quenched from high temperatures, a procedure that may suggest better homogeneity. Therefore, it would be interesting and useful to obtain  $H_{c2}(\delta)$  values by applying this fluctuation analysis to quenched epitaxial thin films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

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<sup>1</sup>R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, *Phys. Rev. B* **36**, 5719 (1987).

<sup>2</sup>V. Z. Kresin, S. A. Wolf, and G. Deutscher, *Physica C* **191**, 9 (1992).

<sup>3</sup>R. McCormack, D. de Fontaine, and G. Ceder, *Phys. Rev. B* **45**, 12 976 (1992).

<sup>4</sup>B. W. Veal and A. P. Paulikas, *Physica C* **184**, 321 (1991).

<sup>5</sup>R. Beyers, B. T. Ahn, G. Gorman, V. Y. Lee, S. S. P. Parkin, M. L. Ramirez, K. P. Roche, J. E. Vazquez, T. M. Gür, and R. A. Huggins, *Nature (London)* **340**, 619 (1989).

<sup>6</sup>T. Zeiske, R. Sonntag, D. Hohlwein, N. H. Andersen, and T. Wolf, *Nature (London)* **353**, 542 (1991).

<sup>7</sup>E. C. Jones, D. K. Christen, J. R. Thompson, R. Feenstra, S. Zhu, D. H. Lowndes, J. M. Phillips, M. P. Siegal, and J. D. Budai, *Phys. Rev. B* **47**, 8986 (1993).

<sup>8</sup>J. Mesot, P. Allenspach, U. Staub, A. Furrer, and H. Mutka, *Phys. Rev. Lett.* **70**, 865 (1993).

- <sup>9</sup>M. Iliev, C. Thomsen, V. Hadjiev, and M. Cardona, *Phys. Rev. B* **47**, 12 341 (1993).
- <sup>10</sup>J. G. Ossandon, J. R. Thompson, D. K. Christen, B. C. Sales, Y. Sun, and K. W. Lay, *Phys. Rev. B* **46**, 3050 (1992).
- <sup>11</sup>S. Ullah and A. T. Dorsey, *Phys. Rev. B* **44**, 262 (1991).
- <sup>12</sup>R. Ikeda, T. Ohmi, and T. Tsuneto, *J. Phys. Soc. Jpn.* **58**, 1377 (1989).
- <sup>13</sup>V. G. Kogan, M. Ledvij, A. Yu. Simonov, J. H. Cho, and D. C. Johnston, *Phys. Rev. Lett.* **70**, 1870 (1993).
- <sup>14</sup>R. Feenstra, T. B. Lindemer, J. D. Budai, and M. D. Gallo-way, *J. Appl. Phys.* **69**, 6569 (1991).
- <sup>15</sup>K. Maki and R. S. Thompson, *Phys. Rev. B* **39**, 2767 (1989).
- <sup>16</sup>Z. Hao, J. Clem, M. McElfresh, L. Civale, A. Malozemoff, and F. Holtzberg, *Phys. Rev. B* **43**, 2844 (1991).
- <sup>17</sup>W. E. Lawrence and S. Doniach, in *Proceedings of the 12th International Conference on Low Temperature Physics, Kyoto, 1970*, edited by E. Kanda (Keigaku, Tokyo, 1971), p. 361.
- <sup>18</sup>S. H. Han, C. C. Almasan, M. C. de Andrade, Y. Dalichaouch, and M. B. Maple, *Phys. Rev. B* **46**, 14 290 (1992).
- <sup>19</sup>M. P. Siegal, J. M. Phillips, A. F. Hebard, R. B. van Dover, R. C. Farrow, T. H. Tiefel, and J. H. Marshall, *J. Appl. Phys.* **70**, 4982 (1991).
- <sup>20</sup>R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck, Jr., and L. W. Rupp, Jr., *Physica C* **165**, 419 (1990).
- <sup>21</sup>J. D. Jorgensen, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, H. Claus, and W. K. Kwok, *Phys. Rev. B* **41**, 1863 (1990).
- <sup>22</sup>J. G. Ossandon, J. R. Thompson, D. K. Christen, B. C. Sales, H. R. Kerchner, J. O. Thomson, Y. R. Sun, K. W. Lay, and J. E. Tkaczyk, *Phys. Rev. B* **45**, 12 534 (1992).
- <sup>23</sup>M. Däumling, *Physica C* **183**, 293 (1991).
- <sup>24</sup>U. Welp, S. Fleshler, W. K. Kwok, R. A. Klemm, V. M. Vinokur, J. Downey, and G. W. Crabtree, in *High Temperature Superconductivity*, edited by S. K. Malik and S. S. Shah (Nova Science, New York, 1992).
- <sup>25</sup>U. Welp, W. K. Kwok, G. W. Crabtree, K. Vandervoort, A. Umezawa, and J. Z. Liu, *Phys. Rev. Lett.* **62**, 1908 (1989).
- <sup>26</sup>This film was grown by the  $\text{BaF}_2$  process and subsequently showed a 2% ion-channeling RBS yield at full oxygenation. However, due to the appearance of a discrete distribution of  $T_c$ 's for  $\delta > 0$ , this sample was not included in the present fluctuation analysis.
- <sup>27</sup>M. S. Osofsky, J. L. Cohn, E. F. Skelton, M. M. Miller, R. J. Soulen, Jr., S. A. Wolf, and T. A. Vanderah, *Phys. Rev. B* **45**, 4916 (1992).
- <sup>28</sup>J. L. Vargas and D. C. Larbalestier, *Appl. Phys. Lett.* **60**, 1741 (1992).
- <sup>29</sup>H. L. Edwards, J. T. Markert, and A. L. de Lozanne, *Phys. Rev. Lett.* **69**, 2967 (1992).
- <sup>30</sup>J. Yu, S. Massidda, A. J. Freeman, and R. Podloucky, *Physica C* **214**, 335 (1993).
- <sup>31</sup>P. B. Allen, W. E. Pickett, and H. Krakauer, *Phys. Rev. B* **37**, 7482 (1988).
- <sup>32</sup>Accepted values for  $H_{c2}(0)(H||c)$  generally occur in the range 1000–1250 kOe as obtained from Refs. 10 and 16.
- <sup>33</sup>M. Lang, R. Kürsch, A. Grauel, C. Geibel, F. Steglich, H. Rietschel, T. Wolf, Y. Hidaka, K. Kumagai, Y. Maeno, and T. Fujita, *Phys. Rev. Lett.* **69**, 482 (1992).
- <sup>34</sup>S. A. Wolf and V. Z. Kresin, *IEEE Trans. Magn.* **27**, 852 (1991).
- <sup>35</sup>M. Däumling, L. E. Levine, and T. M. Shaw, in *Advances in Cryogenic Engineering (Materials)*, edited by F. R. Fickett and R. P. Reed (Plenum, New York, 1992), Vol. 38, p. 949.
- <sup>36</sup>A more recent Hao *et al.* analysis of the previously published data of Ref. 22.