Type-II to type-I transition in superconducting, sputtered $ErRh_4B_4$ films

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High-quality films of both the body-centered and primitive tetragonal phases of $ErRh_4B_4$ have been made by dc sputtering. Critical fields perpendicular and parallel to these films have been measured. The major result of this research is the interpretation of these measurements for the reentrant superconducting primitive phase. It is concluded that a type-II to type-I transition occurs as temperature T falls below about 2.4 K. In this way the large apparent discrepancy between parallel and perpendicular critical fields can be understood as being due to the intermediate state. The analysis also indicates that the superconducting condensation energy E_c is non-BCS and falls to a low value at the reentrant transition. However, it is necessary to extrapolate Landau parameters for the magnetic normal state to determine E_c, so that this conclusion is not definite. The critical field at the upper transition temperature is reported to have an anomalous, and as yet unexplained, temperature dependence.

I. INTRODUCTION

The discovery[1] of materials which exhibit both magnetic and superconducting order has led to considerable experimental and theoretical activity. The coexistence of ferromagnetism and superconductivity discovered in $ErRh_4B_4$ has offered an interesting challenge to theorists, and a number of models have been proposed.[2,3] It is the intention of this paper to investigate the extent to which critical-field measurements in thin films of $ErRh_4B_4$ can shed light on some of the basic assumptions and conclusions of these models.

There are several questions which do not seem to be fully resolved at this time. Why is the reentrant transition at T_{c2} (For $H=0$) first order when ferromagnetic and superconducting transitions in zero field are known to be second order? Is the common assumption valid, that the effect of exchange between the localized spins and the superconducting electrons is just[3] to renormalize certain parameters [$H_c(0)$, T_c, etc.] in the BCS theory? Is there, as suggested by Tachiki *et al.*,[3] a transition from type-II to type-I superconductivity as the temperature is lowered? In the case of thin films, why are the parallel and perpendicular critical-field measurements of Cantor *et al.*[4] incompatible at low temperatures?

In this paper, the above questions will be addressed as well as some new features of our measurements of critical fields in sputtered films of $ErRh_4B_4$. The paper is organized in the following manner. Section II is devoted to our sample preparation and characterization. These samples include films of both phases of $ErRh_4B_4$, the primitive tetragonal (pt) which is a reentrant ferromagnetic superconductor and the body-centered tetragonal (bct) which is a coexistent antiferromagnet and superconductor. Section III discusses the measurement techniques and results for the critical fields of the pt phase while the bct results are deferred until Sec. IX for clarity of presentation.

In order to compare the perpendicular and parallel measurements, the magnetization must be determined independently. This is done in Sec. IV with the aid of Landau parameters determined previously for bulk polycrystalline $ErRh_4B_4$. A discrepancy is found, which is similar to that measured by Cantor *et al.*[4] In Sec. V we offer a new explanation based on a transition from type-II to type-I superconductivity *and* the reduced critical field of the intermediate state of a type-I superconductor. Section VI outlines the theory of the intermediate-state critical field, showing how this quantitatively explains the above discrepancy using only a single parameter which is determined independently. In Sec. VII the superconducting condensation energy is calculated using the Landau parameters and the measured critical fields. Because it is in disagreement with popular assumptions, the implication of this result as well as a discussion of possible problems in this analysis is included. Near the upper transition temperature, the critical fields behave anomalously, and this is discussed in Sec. VIII. Finally, Sec. IX gives the preliminary measurements on the bct phase of $ErRh_4B_4$, while Sec. X summarizes the conclusions and directions for future work.

II. SAMPLE PREPARATION AND CHARACTERIZATION

The films of $ErRh_4B_4$ were made by dc sputtering and characterized by x rays, residual resistance ratio (RRR), superconducting transition temperatures and widths, and the angular dependence of the critical field. This latter measurement shows there is no preferred orientation in the films.

The use of a Plasmax triode sputtering source allowed independent manipulation of discharge current and target potential. A stoichiometric target (0.7 in. diam) was prepared in an induction furnace, and the x rays revealed the primitive tetragonal structure with small amounts or RhB impurities. In total, 15 films were deposited onto heated single-crystal sapphire substrates with temperatures ranging from 800 to 950 °C. This temperature was measured by placing another substrate on the heater and mechanically mounting a thermocouple to the surface. Typical vacuum in the cryopumped chamber prior to sputtering was 3×10^{-7} Torr with the heater on. Argon pressure ranged from 2 to 5 mTorr and 4500-Å films were obtained after ~20 min sputtering time with a 400-V target potential.

X-ray diffraction measurements revealed that some of the films had the pt $ErRh_4B_4$ structure with lattice constants similar to bulk values. Other films surprisingly displayed the bct structure which had only been found[5] in Ru-doped samples until recently.[6] These two phases have nearly identical x-ray spectra except in the region of 2θ equal to 34° and 40°, as shown in Fig. 1. Extrapolation of the bct lattice constants of Ref. 5 to zero Ru concentration indicates that the allowed reflections near 34° and 40° will not be resolved and appear as single peaks. Films which showed single peaks at these angles such as $ErRh_4B_4$ no. 1 did not display reentrant superconductivity as will be discussed later. The primitive tetragonal structure has well-resolved doublets near 34° and 40°, and such films always showed reentrant behavior in zero applied field as in Fig. 2. It is not exactly clear which sputtering parameters determine the phase obtained; however, the pt structure was generally correlated with higher substrate temperatures. The complete absence of any x-ray doublet structure in the $ErRh_4B_4$ no. 1 film indicates it is essentially single-phase bct with little or no pt phase present. The converse cannot be said of the pt $ErRh_4B_4$ no. 14 film using x-ray data alone. However, below the reentrant temperature the full normal-state resistance (see Fig. 2) is recovered, indicating that the amount of superconducting bct phase is negligible.

Superconducting transition temperatures measured resistively are near bulk values for the better films (e.g., the midpoint of $ErRh_4B_4$ no. 14 is at 8.22 K, the width ~0.06 K, and $r_R=3.6$, where r_R is the residual resistance ratio). These T_c's correlate directly with RRR in a similar fashion to the work of Rowell *et al.*[7]; that is, films with $r_R\geq3$ have the highest T_c. The T_c for the bct phase samples was somewhat lower (e.g., $ErRh_4B_4$ no. 1 was 7.65 K,

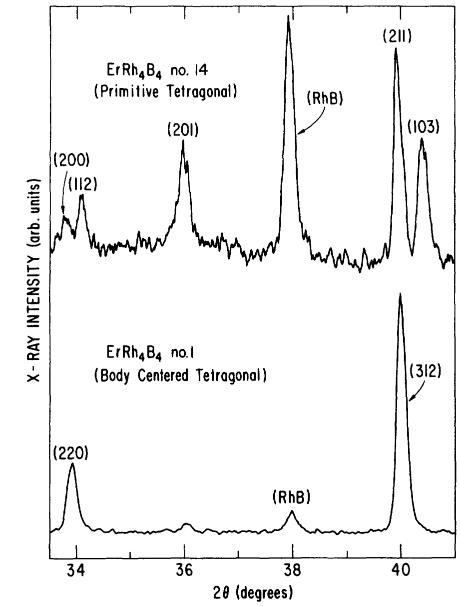

FIG. 1. Partial x-ray spectrum in a θ-2θ scan of the $ErRh_4B_4$ films used in this study. The primitive tetragonal (top) shows the characteristic doublets.

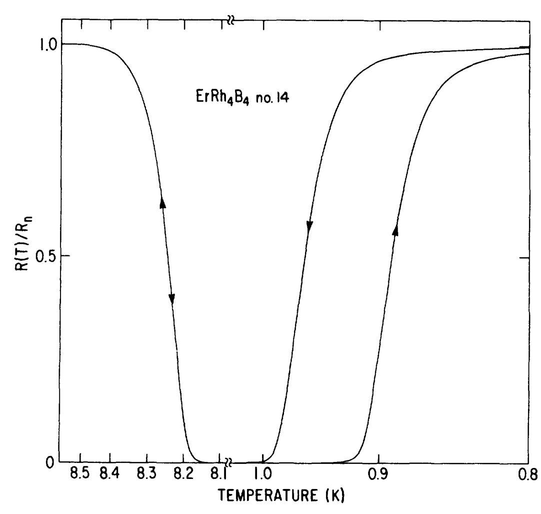

FIG. 2. Zero-field transitions of the primitive tetragonal $ErRh_4B_4$ showing the usual superconducting transition at $T_{c1}\cong8.22$ K, and the hysteretic reentrant transition at $T_{c2}\simeq0.925$ K. Note that essentially 100% of the normal-state resistance is recovered below T_{c2}.

width 0.06 K, and $r_R = 3.3$).

Figure 1 indicates that RhB impurities are present in both the pt and bct films although x-ray intensity cannot be used to determine the percentage. Because of the overall quality of the films we estimate a maximum possible RhB concentration of 20%. Such an impurity is neither superconducting nor magnetic and therefore should not have a dramatic effect on the properties of these films.

It is now known from single-crystal measurements[8] that the magnetic properties of $ErRh_4B_4$ (primitive) are highly anisotropic and this is observed in the superconducting critical fields. Therefore, an important characteristic of these films is the degree (if any) of preferred orientation. Although Rheed camera x rays have been used to this end, the large magnetic anisotropy [at 4.2 K, B_c (c axis)/B_c (a axis)$\cong$2.4] provides an alternative simple and sensitive method.

Consider a thin film with an applied field H_a at an arbitrary angle θ with respect to the normal. If H_a is decomposed into parallel and perpendicular components, the usual boundary conditions can be applied (we assume no surface superconductivity[4]), and one finds

$$\frac{1}{H_a^2(\theta)} = \frac{\cos^2\theta}{B_{\text{int}}^2(\theta)} + (1+4\pi\chi_{||})^2 \frac{\sin^2\theta}{B_{\text{int}}^2(\theta)} , \quad (1)$$

where $B_{\text{int}}(\theta)$ is the internal induction and $\chi_{||}$ is the susceptibility for a parallel field. If the film is isotropic, then the critical applied field $H_{ac}(\theta)$ must be given by Eq. (1) with a single critical value of B_{int} for *all* values of θ. This relation can be written compactly using the special cases of $\theta = 0,90°$ as

$$\frac{1}{H_{ac}^2(\theta)} = \frac{\cos^2\theta}{B_{c\perp}^2} + \frac{\sin^2\theta}{H_{c||}^2} . \quad (2)$$

It should be pointed out that a similar form has been derived[9] for the case of an intrinsic anisotropic critical field, as might occur in single crystal $ErRh_4B_4$ or layered films.[10]

Therefore, the angular dependence of the critical field was measured in the $ErRh_4B_4$ (primitive) film. The applied field was increased monotonically in steps and the film rotated through 360° while the resistance was measured. Thus we measure $R(\theta)$ for various values of H_a in a helium bath at 4.2 K. We use the criterion of $R(\theta)$ equal to 50% of its normal value to define $\theta_c(H_a)$ or $H_{ac}(\theta)$. These are shown in Fig. 3 to be in excellent agreement with Eq. (2). In addition, rotating the film in its plane indicated less than 2% variation in $H_{ac}(\theta)$. These results provide strong evidence of a polycrystalline film with random orientation of the grains. We also conclude that any anisotropy in the critical fields is caused *only* by differences in electromagnetic boundary conditions.

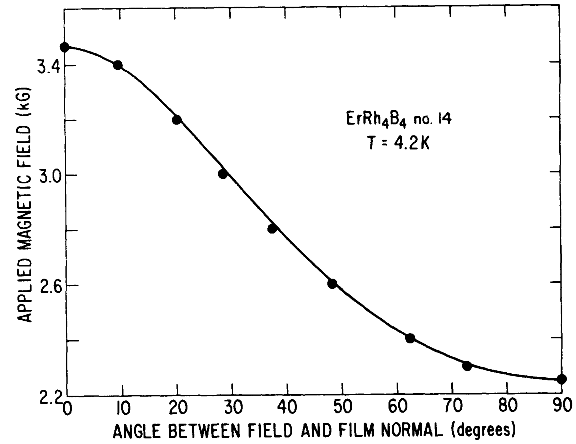

FIG. 3. Critical field of primitive tetragonal $ErRh_4B_4$ as a function of angle θ with respect to the film normal. Solid curve is a prediction based on a polycrystalline film with randomly oriented grains.

III. MEASUREMENT OF CRITICAL FIELDS

As pointed out in the Introduction, an important part of this study involves investigations of the nature of the hysteretic reentrant transition of the primitive tetragonal $ErRh_4B_4$ at T_{c2} in the presence of a magnetic field. For this reason, and also because careful critical-field measurements are desired in general, any hysteresis due to the applied magnetic field must be scrupulously avoided. Therefore, during every low-temperature experiment the field was raised *monotonically* to avoid inconsistencies due to trapped flux in the magnet, solder joints, or contacts. In order to minimize flux pinning effects in the films, the field was always increased while the film was in the fully normal state, i.e., above T_{c1} or below T_{c2}. This provided consistent results upon repeated cycling through the transition. As a consequence, the experiments consisted of measuring resistance versus temperature, and examples of these are shown in Fig. 4.

Because of the demagnetizing factor, an applied field perpendicular to a thin film determines the internal induction B whereas a parallel applied field gives the internal H field. While the traces in Fig. 4 of $R(T)$ for $H_{||}$ look quite regular, there is a more complicated structure for $B_\perp$. Although this added feature was only found in a narrow range of perpendicular fields (2–3 kG), it underlines one of the drawbacks of resistive transitions: They focus on a small part of the sample left superconducting after most of the sample is normal. For example, if one is

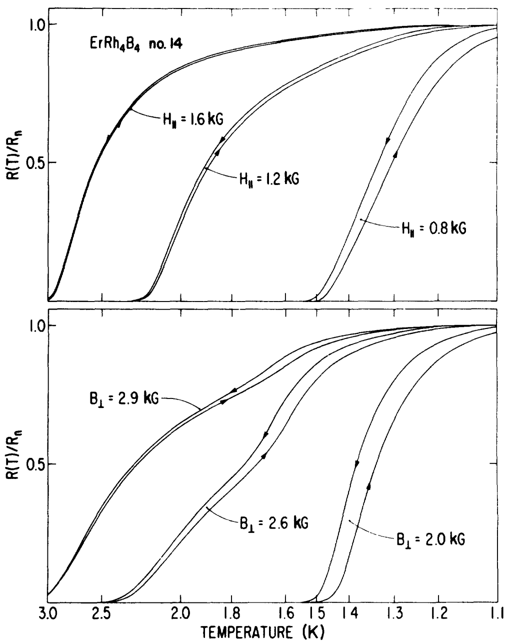

FIG. 4. Resistive transitions of a primitive tetragonal $ErRh_4B_4$ film as the temperature is slowly swept, for various applied fields perpendicular (bottom) and parallel (top) to the films.

dealing with a random two-dimensional percolation network, resistance would *first appear* when 50% of the sample is normal. In the case of these films of thickness 0.5 μm, three-dimensional percolation is probably more appropriate so that there will be no measurable resistance when half the film is normal. However, for present purposes, the customary midpoint (half the normal-state resistance) will be used to define $T_c(H)$ and the results are shown in Fig. 5.

The $R(H)$ data was also analyzed using the criterion of 1% of the normal resistance to define $T_c(H)$. This had little effect on the reentrant primitive tetragonal sample: T_{c1} and T_{c2} were slightly smaller and larger, respectively, and the critical fields at intermediate temperatures were reduced about 10%. On the other hand, there was a significant difference for the bct sample which will be discussed further in Sec. IX.

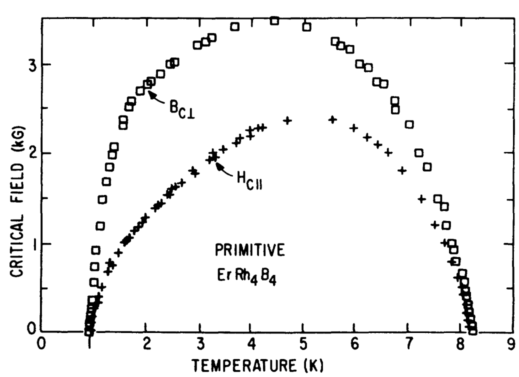

FIG. 5. Temperature dependence of the midpoint of the transition for the primitive tetragonal $ErRh_4B_4$ film in various fields: parallel (plus) and perpendicular (square).

Because of the known anisotropy[8] of the critical field for the pt phase, the *actual percolation path* determining the resistive transition should depend on the orientation of the field. However, the variation of the critical applied field, upon rotating the sample (both in and out of the plane of the film—see Sec. II and Fig. 2), indicates that the transition is independent of the percolation path. This is no doubt because the large critical field along the c axis is reduced considerably for only a few degrees of misalignment.[11] In addition, the variation in the basal plane of the two equivalent a axes is expected to be much smaller.[12] Therefore, in a randomly oriented polycrystal, grains with a large critical field (c axis approximately parallel to H_a) are a small part of the sample for *any* orientation of H_a. As such these grains merely contribute an unconnected collection of superconducting grains in the otherwise normal matrix when $H_a > H_{ac}$. For example, note that the resistive transitions in a field never recover the full normal resistance until $T \sim T_{c2}$ (see Fig. 4). Further evidence that these grains have a small effect is the approximate agreement of $H_{c\parallel}$ (see Fig. 5) with the a-axis single-crystal critical fields[8] in both magnitude *and* temperature dependence. For the same reason these grains have a small effect on magnetization measurements (note that the c-axis susceptibility is very small[8]). Thus the observed χ for the polycrystal[13] and single crystal[8] a axis are almost the same. We conclude that although there may be small effects due to the different polycrystal averages involved in our $H_{c\parallel}$ measurements and the magnetization measurements,[13] they both reflect closely the behavior of the single-crystal a axis.[8]

In the absence of surface superconductivity,[4] a superconductor with a paramagnetic normal state is expected to have a larger perpendicular critical field $B_{c\perp}$ than its parallel critical field $H_{c\parallel}$, by an amount equal to the magnetization. This qualitatively explains the difference shown in Fig. 5, and was first pointed out by Cantor *et al.*[4] Sections IV–VI reconcile the differences in Fig. 5 *quantitatively.* The experimental results reported in Ref. 4 were qualitatively similar to Fig. 5; however, the magnitudes of $H_{c\parallel}$ and $B_{c\perp}$ reported *here* are considerably smaller and closer to the values determined by magnetization in polycrystal[14] and single-crystal[8] (a-axis) bulk samples.

In cases where hysteresis is found, $T_c(H)$ is taken as the average of the two midpoint temperatures, and the difference in midpoint temperatures divided by the average is taken as a measure of the hysteresis (supercooling-superheating). The hysteresis is shown in Fig. 6. Contrary to the critical field, the hysteresis does not depend on the orientation nor magnitude of the applied field. In spite of the scatter at higher temperatures, the natural conclusion from the data is that the hysteresis depends only on temperature even though $B_{c\perp}$ is 2 to 4 times larger than $H_{c\parallel}$ in this range. The hysteresis is also seen to decrease rapidly and approach zero between 2 and 3 K. Measurements of $B_{c\perp}$ and $H_{c\parallel}$ for the bct phase of $ErRh_4B_4$ were made in the same way; however, the preliminary results and discussions are deferred until Sec. IX for clarity of presentation.

IV. CALCULATION OF $B_{c\parallel}$ FROM $H_{c\parallel}$

In order to test whether the magnetization can fully explain the differences in $B_{c\perp}$ and $H_{c\parallel}$ shown in Fig. 5, an independent determination of the magnetization is needed. Because of the complexities of the low-energy magnetic states due to crystal-field effects, the simple Brillouin function is inadequate.[12] However, the magnetization has been experimentally determined above 0.95 K for bulk polycrystalline $ErRh_4B_4$ by Behroozi *et al.*[13] If the Helmholz free energy of the magnetic *material* is written as

$$F_{nM}-F_{n0}=\frac{\alpha}{2}M^2+\frac{\beta}{4}M^4+\frac{\gamma}{6}M^6 , \tag{3}$$

then Behroozi *et al.*[13] find the Landau parameters to be given by $\alpha=\alpha_0(T-T_m)$, $\beta\approx 0$, and $\gamma\cong\gamma_0(1+2T)$, where $\alpha_0\cong 5.5\ \mathrm{K}^{-1}$, $T_m\cong 0.95$ K, and $\gamma_0\cong 0.33\times 10^{-10}\ \mathrm{G}^{-4}$. By differentiation one obtains

$$H=\frac{\partial F}{\partial M}=\alpha M+\gamma M^5 , \tag{4}$$

so that $M_{c\parallel}$ can be determined from $H_{c\parallel}$ by iteration of Eq. (4), and finally

$$B_{c\parallel}=H_{c\parallel}+4\pi M_{c\parallel} . \tag{5}$$

For temperatures above 4 K the magnetization is small and ferromagnetism is out of the question. In addition, the superconducting transition in a field is second order (i.e., shows no hysteresis) which indicates a type-II superconductor. Under these circumstances, $B_{c\parallel}$ calculated from Eqs. (4) and (5) must equal the measured $B_{c\perp}$ (see Sec. II). In order to force this agreement, α_0 must be taken as adjustable and increased by 30% to $7.2\ \mathrm{K}^{-1}$. For example, this could be due to disordered regions with lower T_m or to nonmagnetic, nonsuperconducting RhB impurities in the film (see Fig. 1).

The results of this *calculation* of $B_{c\parallel}$ are shown in Fig. 7 along with the *measured* $B_{c\perp}$. There is clearly a considerable discrepancy at lower temperatures, and it cannot be resolved by adjusting the Landau parameters.

V. DISCREPANCY BETWEEN $B_{c\perp}$ AND $B_{c\parallel}$ AT LOW T

The discrepancy between $B_{c\perp}$ and $B_{c\parallel}$ at low T shown in Fig. 7 is qualitatively the same as reported by Cantor *et al.*,[4] but is much larger. Our use of the experimentally determined Landau parameters rather than the Brillouin function to calculate $B_{c\parallel}$ no doubt accounts for the difference in magnitudes of the discrepancy. Cantor *et al.*[4] proposed that ferromagnetic correlations cause the discrepancy; however, we propose a *new* explanation based on a transition from type-II superconductivity at high T to

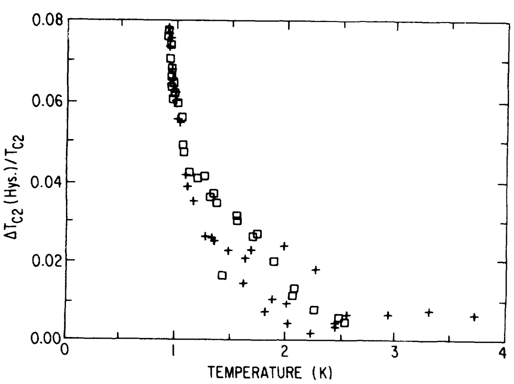

FIG. 6. Hysteresis in the resistive transitions (as defined in the text) for the primitive tetragonal $ErRh_4B_4$ film in parallel fields (plus) and perpendicular fields (square).

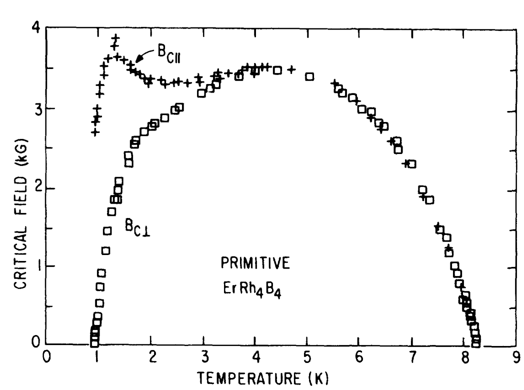

FIG. 7. Comparison of $B_{c\perp}$ (square) measured and $B_{c\parallel}$ (plus) calculated from the measured $H_{c\parallel}$.

type-I superconductivity at low T. The theoretical basis of such a transition has been discussed by Tachiki *et al.*[3] and there is experimental evidence in the magnetization measurements of polycrystal[15] and single crystal[16] $ErRh_4B_4$.

If the superconductor is type I, then a perpendicular field less than $B_{c\perp}$ will result in an intermediate state composed of macroscopic sized (much greater than ξ, λ) regions of normal and superconducting phases coexisting. The intermediate-state critical field B_{cI} can be substantially reduced[17] from the thermodynamic critical field or in this case $B_{c\parallel}$. This reduction can be especially large for a paramagnetic normal state, as will be shown in Sec. VI.

Such an explanation of our data has additional implications. The hysteresis of Fig. 6 occurs over roughly the same temperature range that the sample is type I. Thus the fact that the reentrant transition is first order (even in zero *applied* field at T_{c2}) may be a *result of* the superconductor being type I. In addition, the theoretical explanations[2] of the coexistence of superconductivity and ferromagnetism generally must make assumptions on whether the superconductivity is type I or type II.

VI. INTERMEDIATE-STATE CRITICAL FIELD

In a closely related paper,[18] one of the authors has shown how to calculate the intermediate-state perpendicular critical field B_{cI} for a type-I superconducting film with a paramagnetic normal state. For a linear relation between H and B, the result can be written explicitly as

$$B_{cI}=B_{c\parallel}\left[\left(1+4\frac{\delta'}{d}\right)^{1/2}-2\left(\frac{\delta'}{d}\right)^{1/2}\right], \tag{6}$$

where $\delta'=(1+4\pi\chi)\delta$, $(1+4\pi\chi)=B/H$, and $\delta=\sigma_{ns}/(H_c^2/8\pi)$ is the usual length associated with σ_{ns}, the interphase surface energy per unit area of boundary between superconducting and normal phases. As shown in Ref. 18, Eq. (6) is valid when there is no spontaneous ferromagnetism and the magnetization is not approaching saturation, i.e., the term γM^5 is small compared to αM. For the perpendicular field measurements, this is rigorously true at all temperatures above T_m because $B_{c\perp}$ is so small (see Fig. 5). Saturation effects can be clearly seen in the parallel field analysis up to about 1.7 K since $B_{c\parallel}$ (and hence $M_{c\parallel}$) is much larger.

The calculation of δ was also outlined in Ref. 18, but even for a linear $H(B)$ relation, an analytical solution is only possible in three special cases: (a) if $\kappa\to 0$, then $\delta\cong 1.89\xi(T)$, (b) if $\kappa\to\infty$, then $\delta\cong -1.104\lambda(T)$, and (c) if $\kappa=1/\sqrt{2}$, then $\delta=0$. Here $\kappa=\lambda(T)/\xi(T)$ and

$$\lambda(T)=\lambda_L(T)/(1+4\pi\chi)^{1/2} .$$

The numerical integration of the Ginzburg-Landau equations to obtain δ for arbitrary κ has not been done here, since it is nontrivial, and the dominant effect of the magnetism comes from the rescaling of δ by $(1+4\pi\chi)$ in Eq. (6). Instead, a simple interpolation scheme is employed, which relies on the special limiting cases, and the observation by Ginzburg and Landau[19] that the first-order correction to the $\kappa=0$ analytical solution of δ/λ is proportional to $\kappa^{-1/2}$. Thus it is easily demonstrated that the special cases and the form of the first-order correction for $\kappa=0$ are contained in the approximation

$$\frac{\delta}{\xi}\cong 1.89-1.32\kappa^{1/2}-1.104\kappa . \tag{7}$$

Thus the calculation of $B_{cI}/B_{c\parallel}$ requires the determination of $\xi(T)$ and $\kappa(T)$ from the critical-field measurements. Independent of paramagnetism in the normal state, the standard result of the GL theory is valid *without rescaling* $\lambda_L(T)$:

$$\xi(T)=\frac{\phi_0}{2\sqrt{2}\pi H_c(T)\lambda_L(T)} , \tag{8}$$

where ϕ_0 is the flux quantum and $H_c(T)$ is the thermodynamic critical field which is related to the condensation energy $E_c=H_c^2/8\pi$. Thus

$$\kappa(T)=\lambda(T)/\xi(T)=\frac{2\sqrt{2}\pi H_c(T)\lambda_L^2(T)}{\phi_0(1+4\pi\chi)^{1/2}} , \tag{9}$$

since $\lambda(T)$ *is* scaled by the paramagnetism.[3]

In the BCS theory[20] $\lambda_L(T)$ and $H_c(T)$ can be related to different integrals[21] over the reduced electronic density of states $\rho(E)$. For the weak coupling BCS theory, the limiting temperature dependences near T_{c1} are $1-t$ for $H_c(T)$ and $(1-t)^{-1}$ for $\lambda_L^2(T)$, where $t=T/T_{c1}$. Thus near T_{c1} Eq. (8) indicates that the GL coherence length $\xi(T)$ is proportional to $(1-t)^{-1/2}$, like $\lambda_L(T)$. However, it would be unwise and incorrect at this point to assume a BCS-type dependence for $H_c(T)$ and $\lambda_L(T)$ because of possible temperature-dependent pair breaking by the magnetic ions. The least restrictive condition necessary to continue the analysis is to make an assumption about how $\lambda_L(T)$ and $\xi(T)$ depend *individually* on the thermodynamic critical field $H_c(T)$. In view of the BCS-type relationship near T_{c1} and Eq. (8), it seems a most reasonable assumption that $\lambda_L(T)$ and $\xi(T)$ will respond in *the same way* to any deviations of $H_c(T)$ from BCS theory. In that case $\kappa(T)$ is independent of $H_c(T)$, and only a single parameter

$$\kappa_0=2\sqrt{2}\pi H_c(0)\lambda_L^2(0)/\phi_0$$

needs to be specified. The temperature dependence of $\kappa(T)$ is then given by

$$\kappa(T)=\frac{\kappa_0}{[1+4\pi\chi(T)]^{1/2}}\left[\frac{\kappa(T)}{\kappa(0)}\right]_{\mathrm{BCS}} =\frac{\kappa_0(T)}{(1+4\pi\chi)^{1/2}}\;, \tag{10}$$

where the weak temperature dependence of $H_c(T)\lambda_L^2(T)$ from the BCS theory is included in $\kappa_0(T)$ and $\kappa(T)$.

If this assumption is incorporated into Eq. (8), the result is

$$\xi(T)=\left[\frac{\phi_0}{2\sqrt{2}\pi\kappa_0(T)H_c(T)}\right]^{1/2}\;, \tag{11}$$

showing that for a type-I superconductor it is also necessary to know $H_c(T)$ to get $\xi(T)$. Fortunately this is readily obtained by extending the analysis of the previous sections. For type-I superconductivity (i.e., $\kappa<1/\sqrt{2}$), H_c is determined by setting equal the Gibbs free energy of the normal magnetic and superconducting states. Because of the intermediate state found in thin films in a perpendicular field, the superconducting free energy can only be evaluated in terms of the measured $H_{c\parallel}$, and then only if $d\gg\xi,\lambda$. These latter conditions are well satisfied in the type-I temperature range. Thus we find

$$H_c^2=H_{c\parallel}^2+4\pi\alpha M_{c\parallel}^2+\frac{20\pi\gamma}{3}M_{c\parallel}^6\;, \tag{12}$$

where $M_{c\parallel}=(B_{c\parallel}-H_{c\parallel})/4\pi$ is determined using the previously introduced Landau parameters. For a nonmagnetic type-I superconductor, $M_{c\parallel}=0$ and the measured $H_{c\parallel}$ equals H_c.

Note that for type-II superconductivity (i.e., $\kappa>1/\sqrt{2}$), the susceptibility is small in our films, so that a linear $H(B)$ relation is a very good approximation, and by analogy to the nonmagnetic case we find

$$H_c=(H_{c\parallel}B_{c\parallel})^{1/2}/\sqrt{2}\kappa(T) =H_{c\parallel}(1+4\pi\chi)/\sqrt{2}\kappa_0(T)\;. \tag{13}$$

Substituting Eq. (13) into Eq. (11) shows that $\xi(T)$ reduces to the usual result of the linearized GL equation at B_{c2} [see Eq. (18)].

Choosing the one parameter κ_0 therefore determines the temperature at which $\kappa(T)=1/\sqrt{2}$ and the transition from type II to type I occurs. There are three pieces of evidence from our measurements which can be used as a guide: (a) There is a very slight but reproducible kink in the $H_{c\parallel}(T)$ data at $T\sim 2.5$ K which is similar to that predicted by Tachiki *et al.*,[3] (b) the hysteresis of the reentrant transition disappears between 2 and 3 K, and (c) the discrepancy between $B_{c\parallel}$ and $B_{c\perp}$ is found for temperatures below about 3 K. In addition, magnetization measurements[15] on polycrystalline bulk samples indicate a type-I superconductor up to about 3 K.

However, a more sensitive method to determine κ_0 is to calculate B_{cI} from Eq. (6) and compare it with $B_{c\perp}$. In this way the best fit is found for $\kappa_0\cong 1.15$, indicating a crossover at $T\simeq 2.35$ K. Considering the large discrepancy between $B_{c\parallel}$ and $B_{c\perp}$, the agreement between B_{cI} and $B_{c\perp}$ shown in Fig. 8 is remarkable and can be taken as a strong confirmation of the type-II to type-I transition. Note that B_{cI} is reduced by as much as a factor of 16 from $B_{c\parallel}$.

VII. CONDENSATION ENERGY

As was mentioned in the Introduction, the determination of the superconducting condensation energy (equal to $H_c^2/8\pi$) as a function of temperature would be an extremely valuable contribution to our understanding of the importance of temperature-dependent pair breaking by the magnetic ions. The results of the preceding section in which H_c is determined from parallel field measurements are shown in Fig. 9; they clearly disagree with the BCS-type dependence of $H_c(T)$ which is also plotted for $T_{c1}=8.22$ K and $H_c(0)=3$ kG. Although magnetization measurements on polycrystal $ErRh_4B_4$ gave a similar result,[15,22] no firm conclusion was drawn due to the unknown effects of the possibly large flux pinning. In our measurements this criticism is weakened by the lack of significant hysteresis throughout most of the temperature range (no doubt due to the demagnetization factor being 0 or 1 in our measurements). This discrepancy with BCS theory implies that a simple rescaling of parameters (T_c, H_c, ξ, etc.) suggested by Tachiki *et al.*[3] is

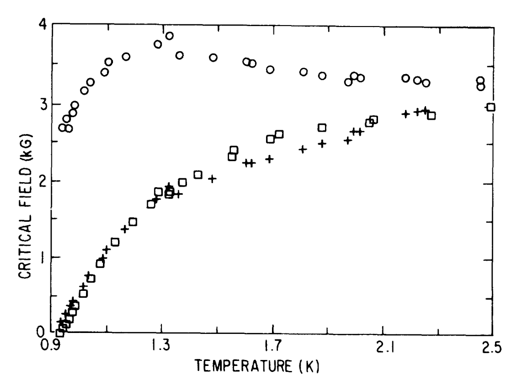

FIG. 8. Data of Fig. 7 are shown for low temperatures along with the intermediate-state critical field B_{cI} (plus) calculated from $B_{c\parallel}$ (circle). The agreement with the measured $B_{c\perp}$ (square) is quite satisfactory.

inadequate to account for the effects of magnetism on the superconductivity in $ErRh_4B_4$.

It should be pointed out that the experimentally determined Landau parameters, introduced in Sec. IV, already define the relationship between $T_m - T_{c2}$ and $H_c(T_{c2})$, since at T_{c2} the Gibbs free energies of the normal and superconducting states must be equal with $H=0$. For the superconducting state ($H=0$)

$$G_{s0}(T_{c2}) = F_{n0}(T_{c2}) - [H_c(T_{c2})]^2/8\pi \,, \tag{14}$$

and for the normal state ($H=0$)

$$G_{n0}(T_{c2}) = F_{nM}(T_{c2}) = F_{n0}(T_{c2}) + \frac{\alpha}{2}M^2 + \frac{\gamma}{6}M^6 \,, \tag{15}$$

where M is the solution of Eq. (4) with $H=0$, i.e., $(-\alpha/\gamma)^{1/4}$. Thus (recalling that α is negative if $T<T_m$),

$$\frac{[H_c(T_{c2})]^2}{8\pi} = \frac{[\alpha_0(T_m - T_{c2})]^{3/2}}{3\gamma^{1/2}} \,, \tag{16}$$

and it *necessarily follows that the condensation energy is small* if T_m is close to T_{c2}.

With the use of $T_m = 0.95$ K and $T_{c2} = 0.925$ K, the value of $H_c(T_{c2})$ from Eq. (16) is about 200 G, in excellent agreement with the extrapolation of the data in Fig. 9 which gives $H_c(0.925\text{ K}) \cong 250$ G. Note that such a small H_c implies a superconducting condensation energy at T_{c2} which is more than *2 orders of magnitude* smaller than its maximum value at about 5 K.

Such a decrease of $H_c(T)$ near T_{c2} is provocative in that it suggests that simple electromagnetic effects[2] may be insufficient to explain the reentrance of $ErRh_4B_4$. For example, for $T \gtrsim T_m$, spin fluctuations may lead to significant pair breaking. However, Eq. (16) shows how sensitive H_c and therefore these conclusions are to the value of T_m. Because of the importance of such a conclusion and the somewhat complex analysis that went into it, we would now like to discuss possible problems in our analysis.

The Landau parameters with $T_m = 0.95$ K were determined by magnetization measurements[13] in the *normal state* of a polycrystal of $ErRh_4B_4$, and are thus expected to correctly predict the ratio of $B_{c\parallel}$ to $H_{c\parallel}$ in our polycrystal films. However, in order to evaluate $H_c(T)$ from Eq. (12), it is necessary to extend the Landau parameters into the field region where they could not be directly measured due to the superconductivity. Thus the fact that magnetic scattering is observed[23] by neutrons at temperatures up to about 1.4 K (on polycrystal $ErRh_4B_4$) in the *superconducting state* ($H_a = 0$), indicates a potential problem in such an extension. On the other hand, the excellent agreement with the calculation of B_{cI} is in part *due to* $H_c(T)$ decreasing as $T \to T_{c2}$ through the dependence of B_{cI} on δ [Eq. (6)], δ on ξ [Eq. (7)], and ξ on $H_c(T)$ [Eq. (11)].

Clearly if the above analysis is repeated for a large value of T_m (say 1.4 K), the value of $B_{c\parallel}$ [and consequently H_c through Eq. (12)] will be larger, especially at lower temperatures. Thus upon changing *only* T_m to 1.4 K (and not α_0 or γ), $H_c(T)$ is found to be roughly constant at 2.6 kG for T below $\sim$4 K and above T_{c2}.

However, as we shall now show, the use of $T_m = 1.4$ K in the previously defined Landau parameter leads to a large inconsistency between the calculated intermediate state B_{cI} and the measured perpendicular $B_{c\perp}$. Unfortunately, the analysis used above for B_{cI} is invalid for $T \lesssim T_m$ because the $H(B)$ relation is nonlinear.[18] Therefore, we first derive a modified analysis which is valid in the limit of small κ and large χ, and thus for the first few experimental points above T_{c2}.

Two crucial steps in the calculation of B_{cI} break down for a nonlinear $H(B)$ relation: (a) The determination of δ is only possible in the limit of small κ so that the magnetic field changes abruptly at the interphase boundary compared to the superconducting order parameter, and (b) in the minimization of the intermediate-state free energy with respect to the normal fraction ρ_n, it is necessary[18] to express $\int_0^{B_{\text{int}}} H\,dB$ explicitly in terms of the internal induction field $B_{\text{int}} = B_a/\rho_n$, where B_a is the applied field.

The smallest measured $H_{c\parallel}$ just above T_{c2} is 32 G, and the above analysis gives $B_{c\parallel} = 5200$ G if $T_m = 1.4$ K. Therefore

$$\kappa \cong \kappa_0 (H_{c\parallel}/B_{c\parallel})^{1/2} \simeq 0.1$$

is small, so that δ can be approximated by its *upper limit* of 1.89 $\xi(T)$. In addition, the large B/H ratio implies that to a good approximation B_{int} is given by $4\pi M_{\text{int}}$, so that the above integral can be evaluated in terms of $M_{\text{int}} \cong B_{\text{int}}/4\pi = B_a/4\pi\rho_n$ as was done in Eq. (12). After the resultant free energy is minimized with respect to ρ_n, the critical field is determined by setting $\rho_n = 1$, in which case,

$$\frac{H_c^2}{8\pi} = 2\left[\frac{\delta}{d}\right]^{1/2} H_c \left[\frac{B_{cI}}{4\pi}\right] + \frac{\alpha}{2}\left[\frac{B_{cI}}{4\pi}\right]^2 + \frac{5\gamma}{6}\left[\frac{B_{cI}}{4\pi}\right]^6 . \tag{17}$$

This equation is then numerically solved for $B_{cI}(T)$ using the $H_c(T)$ determined by the previous analysis for $T_m = 1.4$ K. This calculation exactly mimics the determination of $B_{c\parallel}$ from $H_{c\parallel}$, except that additional terms appear for a perpendicular field due to the interphase boundary and the field energy outside the film.[18]

The values of B_{cI} thus calculated are much too large: about 1.9 and 1.0 kG for $T_m = 1.4$ and 1.2 K, respectively, whereas $B_{c\perp}$ is only 25 G at the same temperature. The biggest weakness in applying this model is the assumption that $\kappa = 0$. However, the actual value of 0.1 for κ would lead to a *smaller value* of δ and hence a smaller reduction in B_{cI}. Thus the disagreement would be even worse.

A second possible problem in the analysis is the assumption about the relationship of $\xi(T)$ and $\lambda_L(T)$ to $H_c(T)$. To test this the entire analysis was again repeated, but with $\lambda_L(T)$ rather than $H_c(T)\,\lambda_L^2(T)$ always given by the *BCS value*. In this second case, deviations in $H_c(T)$ from BCS theory are borne entirely by $\xi(T)$ through Eq. (8). However, using this new assumption made no significant change in the low-temperature results. Thus the calculation of B_{cI} was in good agreement with $B_{c\perp}$ for $T_m = 0.95$ K, but the disagreement for $T_m = 1.4$ K was similar to that for the initial assumption.

The ultimate point is that one cannot explain the perpendicular critical-field measurements using the intermediate-state model if T_m is significantly larger than 0.95 K. Then accepting the excellent agreement shown in Fig. 8 as strong evidence for the validity of this model, we are forced to the conclusion that the superconducting condensation energy (or H_c shown in Fig. 9) is non-BCS type and drops to a small value at the reentrant transition (T_{c2}). However, because of uncertainties resulting from extending the Landau parameters, a definite conclusion about $H_c(T)$ may be unwise at this time.

It should be pointed out that the determination of $H_c(T)$ or the superconducting condensation energy by other methods (such as magnetization[15,22]) will have a similar problem of establishing the correct free energy of the magnetic state in the absence of superconductivity. However, a similar analysis for a single crystal would be most interesting to establish, for example, the effect of polycrystal averages on the above measurements.

VIII. CRITICAL FIELDS NEAR T_{c1}

We now present a discussion of the critical fields near T_{c1}. Figure 10 shows the behavior of $T_{c1}(H)$ for small fields applied parallel to the film. This behavior is anomalous—normally $T_c(H)$ decreases linearly for small H in both type-I and type-II superconductors. Although inhomogeneities can smear this out, they make the structure *less sharp* than linear, whereas the data in Fig. 10 are clearly sharper, in fact almost vertical (T_c independent of H). In perpendicular fields this effect is less pronounced, although still anomalous. To help rule out possible experimental artifacts causing this behavior, measurements were taken by monotonically increasing $H_{\parallel}$ in small steps and cycling back and forth between the transitions at T_{c1} and T_{c2}. Figure 11 shows that the reentrant transition at T_{c2} is strongly dependent on $H_{\parallel}$ for the same values for which T_{c1} is almost independent of $H_{\parallel}$.

This behavior has implications for the GL coherence length which, in a type-II superconductor, is given by

$$\xi^{-2}(T) = \frac{2\pi B_{c2}(T)}{\phi_0} . \tag{18}$$

Since there is no region of a linear dependence of $H_{c\parallel}$ (and hence $B_{c\parallel} = B_{c2}$) on T even for higher fields than shown in Fig. 10, it is clear that ξ does not diverge in the usual manner (i.e., $\xi^{-2} \alpha 1 - t$). It

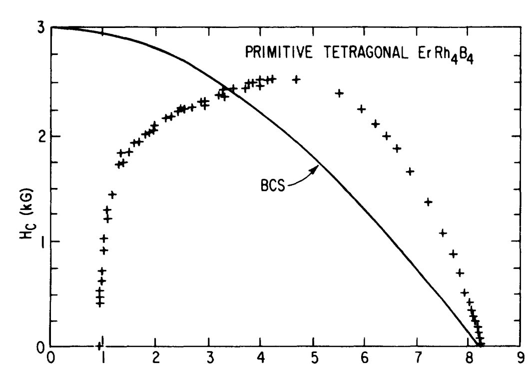

FIG. 9. The thermodynamic critical field (plus) for the primitive tetragonal $ErRh_4B_4$ film determined by the analysis in the text. The solid curve is the BCS dependence for $T_c = 8.221$ K and $H_c(0) = 3$ kG.

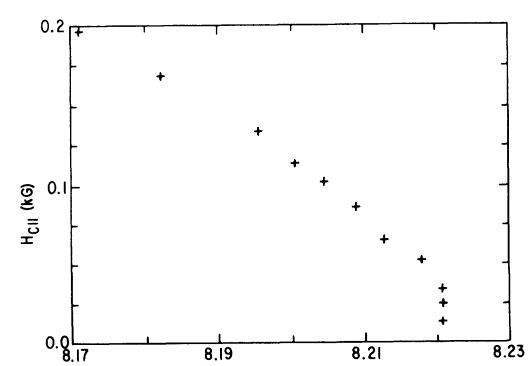

FIG. 10. Parallel critical field for the primitive tetragonal $ErRh_4B_4$ film near T_{c1} showing anomalous behavior at very small fields.

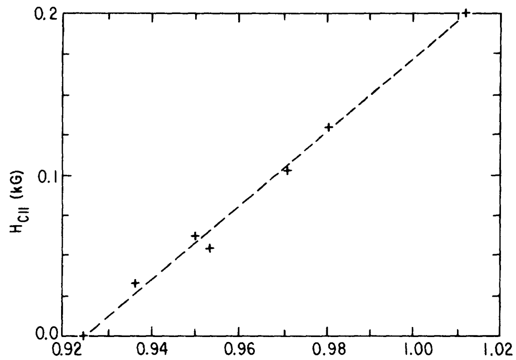

FIG. 11. Parallel critical field for the primitive tetragonal $ErRh_4B_4$ film near T_{c2} showing linear dependence (solid line) on temperature.

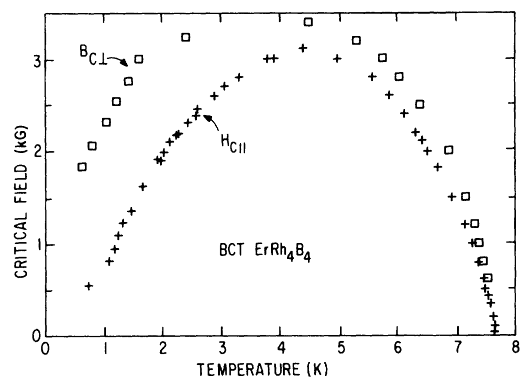

FIG. 12. Temperature dependence of the critical field (1% of normal resistance criterion) for the body-centered-tetragonal $ErRh_4B_4$ film for perpendicular fields (square) and parallel fields (plus).

also follows from Eq. (13) that $H_c(T)$ does not have the $1-t$ dependence found in the BCS theory.

However, a different assumption about how ξ and λ depend on H_c can profoundly affect $H_c(T)$ near T_{c1}. For example, if $\lambda_L(T)$ is assumed to be given by the BCS dependence, then $\kappa(T)$ is no longer given by Eq. (10), and $H_c(T)$ goes linearly to zero at T_{c1}. However, the resulting BCS extrapolation of these data to low temperatures gives $H_c(0)=6.3$ kG, which is considerably higher than the 2.6 kG found in our analysis of the low-temperature data for the same assumption about $\lambda_L(T)$ (see Sec. VII). In addition, the behavior of $\kappa(T)$ is then anomalous: It becomes very large (~ 10 compared to $\kappa_0=1.15$) near T_{c2} because $\xi(T)$ is diverging more slowly than $\lambda(T)$. In any event, the critical fields near T_{c2} in $ErRh_4B_4$ (primitive) are not well understood, but could be an important clue in discovering the interaction between magnetism and superconductivity in this very interesting material.

IX. bct $ErRh_4B_4$

The films of $ErRh_4B_4$ which exhibit the body-centered-tetragonal crystal structure have also been studied, although the investigation is much more preliminary. Figure 12 shows $B_{c\perp}$ and $H_{c\parallel}$ for our best film (narrowest ΔT_c). Note that it is not reentrant in zero field. It is natural to assume that this material is a coexistent superconductor and antiferromagnet like the bulk samples showing this crystal structure (in bulk this phase has been stabilized[5] by the addition of 5% or more Ru for Rh and more recently[6] without Ru).

It should be pointed out that the difference between the 1% and 50% criterion on $R(T)/R_n$ was significant. The data for the midpoint criterion (not shown in Fig. 12) indicated $H_{c\parallel} > B_{c\perp}$ for $3.5 < T < 5.5$ K, and much higher critical fields especially at low temperatures. Because of these problems and the possibility of a type-I transition, the determination of X from these data is of questionable value.

There is a very recent report of stabilization of the bct phase of $ErRh_4B_4$ in a bulk polycrystal.[6] The resistively measured zero-field transition temperature of 7.15 K is somewhat lower than ours (~ 7.65 K), but the critical fields extend to values more than 4 times our highest value. We do not feel that this discrepancy can be explained by pt impurities displaying reentrant superconductivity and thus lowering the critical field of our films. This is because of the x rays (see Fig. 1 and Sec. II) *and* the fact that the low-temperature transitions for the bct films showed no hysteresis, which was always seen in the reentrant pt phase. Therefore, the resolution of this discrepancy may require further experimentation.

X. SUMMARY OF CONCLUSIONS AND FUTURE DIRECTIONS

An important result of this work is the development of a sputtering technique to make high-quality films of both phases (bct and pt) of $ErRh_4B_4$. The x-ray and critical-field measurements indicate these are good polycrystal films with only small amounts of impurity phases. Preliminary critical-field measurements for the bct phase are reported, but the major effort of this research concentrated on the reentrant superconducting pt phase.

Perhaps the most important conclusion is that a type-II—type-I transition occurs in the primitive tetragonal reentrant phase of $ErRh_4B_4$ as predicted by Tachiki *et al.*[3] The excellent agreement of $B_{c\perp}$ with the predictions of the intermediate-state model shown in Fig. 8 offer strong confirmation of this conclusion. Complementary evidence is seen in the experimental $H_{c\|}(T)$ data showing the predicted kink[3] and the hysteresis of the transition. Because this hysteresis disappears for type II, it can be speculated that the first-order character of the reentrant transition at T_{c2} may be a *result of* the superconductor being type I. It would be interesting to see how this reentrant transition would be modified for a type-II superconductor, but a divergent Curie-Weiss susceptibility probably precludes this possibility. The crossover temperature at which the type-II to type-I transition occurs depends on κ_0. Thus if κ_0 *alone* could be changed by, say, impurity content, the crossover temperature should vary. In addition, the analysis of the resulting intermediate state[18] at low temperatures explains the discrepancy observed by Cantor *et al.*[4]

A second important conclusion concerns the attempted determination of the superconducting condensation energy E_c in the pt phase. The analysis for our sputtered films indicates that $E_c(T)$ is not BCS-type and there seems to be a good case for concluding that E_c at the reentrant transition at T_{c2} drops to a very small value relative to its maximum value. However, because of uncertainties in extrapolating the Landau parameters, a definite conclusion about $E_c(T)$ is difficult to make. This appears to be an intrinsic problem in the determination of $E_c(T)$ by other methods such as magnetization. Therefore, a more direct measurement on the superconducting state such as tunneling may be necessary to extract $E_c(T)$ experimentally and to check the assumptions of various theoretical models.[2,3]

The measured critical fields near T_{c1} are clearly anomalous compared to ordinary type-I or type-II superconductors. Careful measurements on bulk polycrystal and single-crystal samples would be important to establish the generality of this effect. The interpretation of this behavior may give new insights about the effect of the magnetism on the superconducting state of $ErRh_4B_4$.

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