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# MAGNETIC AND SUPERCONDUCTING TRANSITIONS IN $Gd_xEr_{1-x}Rh_4B_4$ AND $Gd_xY_{1-x}Rh_4B_4$ †

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## ABSTRACT

The magnetic and superconducting transition temperatures and upper critical fields have been measured for $Gd_xEr_{1-x}Rh_4B_4$ and $Gd_xY_{1-x}Rh_4B_4$. The pressure dependence of $T_c$ for the Er system for $x \leq 0.05$ is $0.5 \times 10^{-2}$ K/kbar. Both systems exhibit reentrant behavior, that is a superconducting transition followed by a magnetic transition at a lower temperature that destroys the superconductivity. For the Er system, the initial additions of Gd actually raise the superconducting critical field followed by the expected decrease for greater additions.

## INTRODUCTION

Recently, an entire new group of ternary borides that exhibit magnetism, superconductivity, or both phenomena has been discovered [1,2]. These new compounds have the general formula $MRh_4B_4$, where M is a three or four valent transition series element. In particular, the compound $ErRh_4B_4$ becomes superconducting at a critical temperature $T_c$ of 8.7 K followed by a return to the normal state at a second critical temperature $T_M \sim 0.8$ K at which long-range ordering of the magnetic moments of the $Er^{3+}$ ions sets in [3]. This compound is the first reentrant superconductor with the magnetic ions distributed periodically in the lattice. To date most of the investigations of magnetic superconductors [4-7] have been limited to systems in which magnetic ions are randomly distributed in a nonmagnetic host. According to Ref. 1, $GdRh_4B_4$ orders ferromagnetically at $T_M = 5.62$ K. As a result, it is desirable to study electronic and magnetic properties of the $Gd_xEr_{1-x}Rh_4B_4$ system. In order to acquire more insight into these materials, we also investigated $Gd_xY_{1-x}Rh_4B_4$ in which $YRh_4B_4$ is a nonmagnetic superconductor with $T_c = 11.3$ K [1]. Other reasons for our choice of Gd as the magnetic impurities are: (1) they exhibit well-defined localized moments resulting in the absence of the complication of spin-density fluctuations; (2) $Gd^{3+}$ is an S-state ion and hence there is no appreciable splitting of the $Gd^{3+}$ $J = 7/2$ multiplet in the crystal field of the surrounding matrices; (3) and the spin of $Gd^{3+}$ is the largest of all of the rare-earth ions.

Since the exchange interaction between two magnetic ions depends on the distance between them, the superconducting transition temperature decreases with increasing Gd concentration. It is similarly desirable to study the variations of $T_c$ with lattice constant by the use of hydrostatic pressures up to 20 kbar.

## EXPERIMENTAL METHOD

The samples were synthesized from high-purity elements by conventional arc melting in a Zr-gettered argon atmosphere. They were then annealed at 1000°C for 1 to 14 days. X-ray analysis on a few samples demonstrated that they possessed the correct crystal structure and lattice constants as determined by Vandenberg and Matthias [2] aside from a few percent of a second unidentified phase as is typical. Conventional four-probe electrical resistance and ac susceptibility techniques were used to determine Tc and $T_M$. We define these temperatures to be the midpoints of the full transitions. Hydrostatic pressures were generated prior to cooling using a one-to-one mixture of isoamyl alcohol and n-pentane by means of the conventional self-clamp technique. We took data at increasing pressures until a maximum pressure of ∿20 kbar was attained, and also took data at decreasing pressures as a check. The magnetic field was provided by a superconducting solenoid.

## RESULTS AND DISCUSSIONS

### I. Upper Critical Field, $H_{c2}$

#### 1. $Gd_xY_{1-x}Rh_4B_4$

As shown in Fig. 1, our data for the sample with x = 0.01 demonstrates, as expected, the monotonic decrease of upper critical field $H_{c2}$ with increasing temperature. For x = 0.03 (not shown) the temperature variation is similar. However, for x = 0.10, as expected, $T_c$ is supressed, but $H_{c2}$ is no longer monotonic and peaks at ∿4 K, suggesting a possibility of reentrant behavior at T ∿1 K. This non-monotonic temperature dependence of $H_{c2}$ may be due to the mechanism described by de Gennes and Sarma [8]. Our brief $Gd^{3+}$ EPR measurements showed that the Gd ions and the conduction electrons couple ferromagnetically. We also made measurements in a $He^3$ cryostat, and found that the sample remains superconducting down to ∿0.5 K in the absence of a field. In the $InLa_{3-x}Gd_x$ system [4] the Gd rich samples also show a non-monotonic temperature variation of $H_{c2}$. As a check on this we ran a sample with $x = 0.2$ and found a $T_c$ of $\sim 7.2$ K and a $T_M$ of 0.59 K (not shown). The 10-90% width of the reentrant transition was quite narrow, 0.065 K. Our temperature dependence of the ac susceptibility is similar to that reported for $ErRh_4B_4$ [3]. Resistivity measurements were not performed on this $x = 0.2$ sample. This unexpected result seems to indicate that reentrant behavior is not a result of a periodic distribution of magnetic ions in the lattices.

2. $Gd_xEr_{1-x}Rh_4B_4$

Using the resistive measurement, we determined the temperature dependence of $H_{c2}(T)$ for $Gd_xEr_{1-x}Rh_4B_4$ system for eleven different values of x ranging from x = 0 to 1. The $x < 0.03$ samples demonstrate the characteristics of a reentrant magnetic superconductor like pure $ErRh_4B_4$ [3] in that they all undergo phase transitions into magnetic states at lower temperatures, $T_M$, at which superconductivity disappears and $H_{c2}$ decreases to zero. Our data for pure $ErRh_4B_4$ (as shown by the inverse deltas) are in agreement with those reported by Fertig, et al. [3]. Surprisingly, the maximum $H_{c2}$ for $x = 0.02$ is even greater than that of pure $ErRh_4B_4$, although this is accompanied by the suppression of $T_c$ and the increase of $T_M$. However, when x is further increased, $H_{c2}$ is lowered until a critical concentration of $x \sim 0.28$ is reached where superconductivity disappears.

In Fig. 3 we show the x dependence of $T_c$ and $T_M$. The suppression of $T_c$ by the introduction of Gd impurities is understandable since our Gd EPR g-shift data provided the information that Gd and Er are strongly ferromagnetically coupled. The solid curve is the result of the Abrikosov-Gorkov (AG) theory [9] relating $T_c$ to x. Our data (as shown by squares) apparently deviate from the AG theory. This deviation may well be due to the Pauli paramagnetic effects, or the quenching of the spin-flip scattering [6], or both. As in the cases of $Gd_xLa_{1-x}$ [10] and $InLa_{3-x}Gd_x$ [11], our $T_M$ is linear in x. Our phase diagram is distinct from those in Refs. 10 and 11, since for $x < 0.28$ $T_M$ falls below $T_c$.

## II. High-Pressure Effects

Recently, Shelton and Johnston [12] reported that both $dT_c/dP$ for $ErRh_4B_4$ and $dT_M/dP$ for ferromagnetic $GdRh_4B_4$, where P is the hydrostatic pressure, are positive. In order to investigate these two competing processes, we have studied $Gd_xEr_{1-x}Rh_4B_4$ with x = 0.03 and 0.05. Figure 4 shows our data for $T_c$. In both cases T increase linearly with P, and $dT_c/dP \approx 0.50 \times 10^{-2}$ (K/kbar) which is identical to that of pure $ErRh_4B_4$ [12]. Apparently, the Gd concentration in our samples is sufficiently dilute that the pressure available was not high enough to cause the strong magnetic coupling as in pure $GdRh_4B_4$, even though they were enough to suppress the superconducting transition temperature.

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† Work performed under the auspices of the Department of Energy.

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## FIGURE CAPTIONS

Fig. 1. Critical field versus temperature for the $Gd_xY_{1-x}Rh_4B_4$ system.

Fig. 2. Critical field versus temperature for the $Gd_xEr_{1-x}Rh_4B_4$ system. Some curves are dashed simply for legibility.

Fig. 3. Superconducting and magnetic phase diagram for $Gd_xEr_{1-x}Rh_4B_4$.

Fig. 4. The effect of pressure on the superconducting transition temperature for $Gd_xEr_{1-x}Rh_4B_4$.

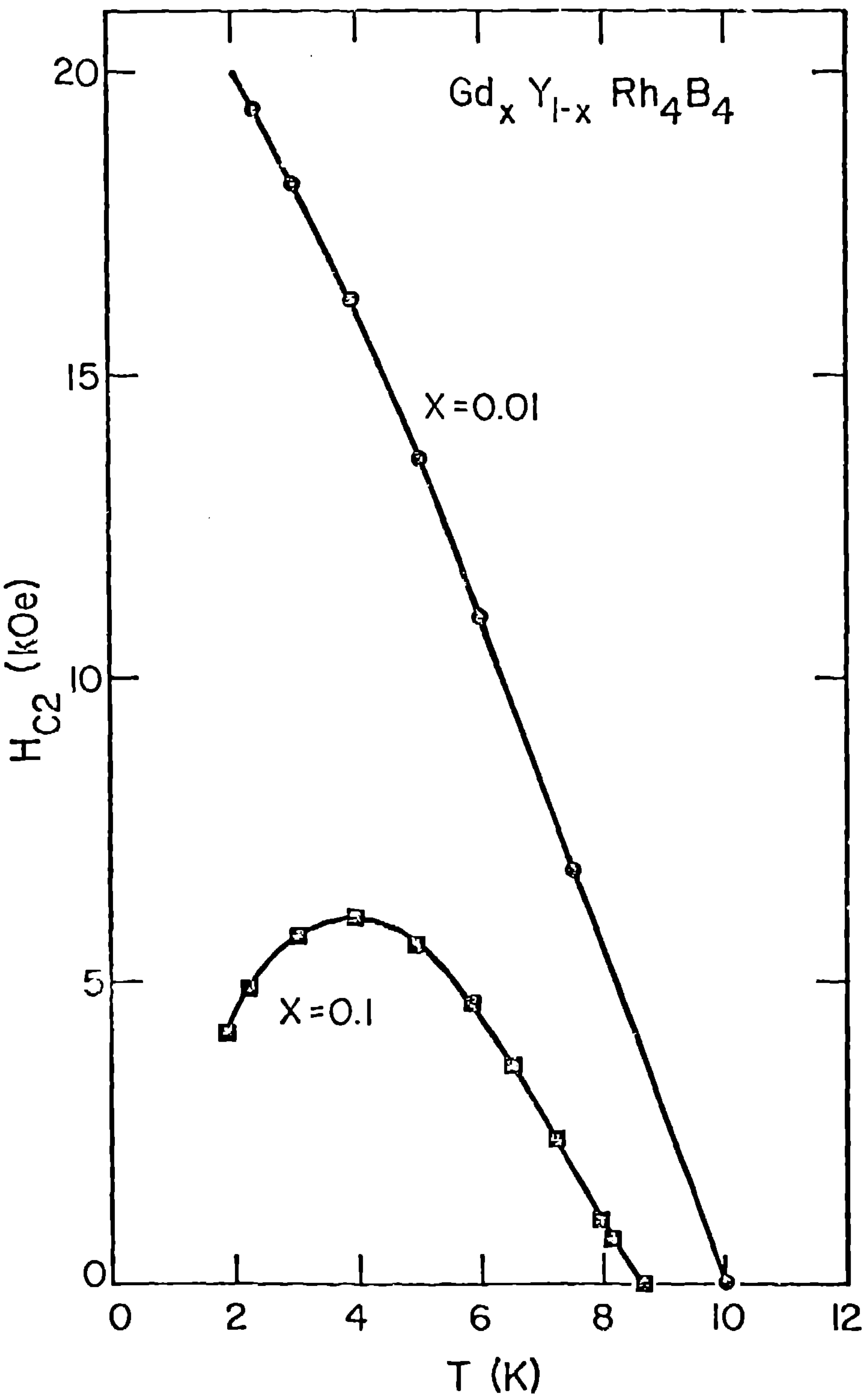
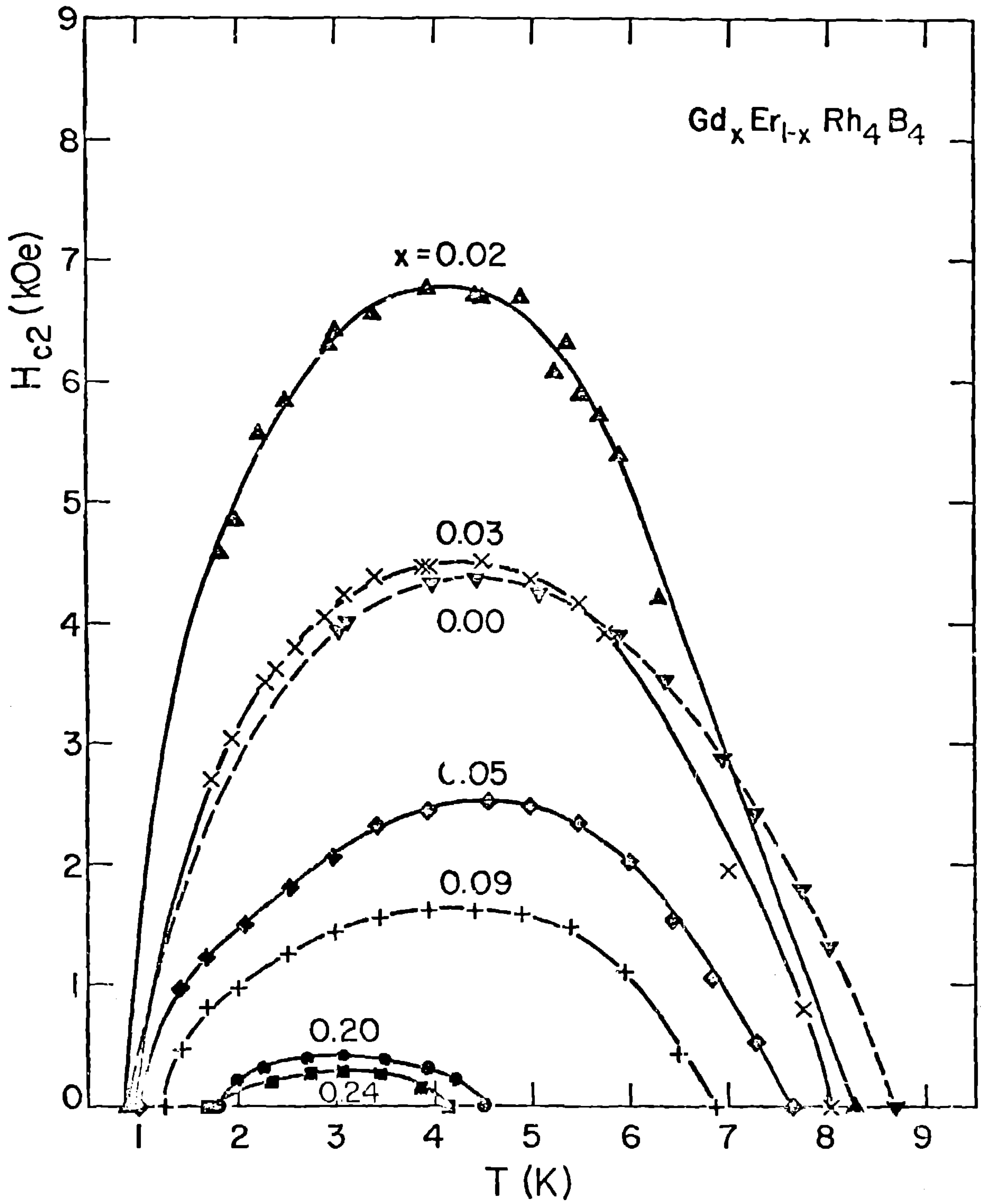
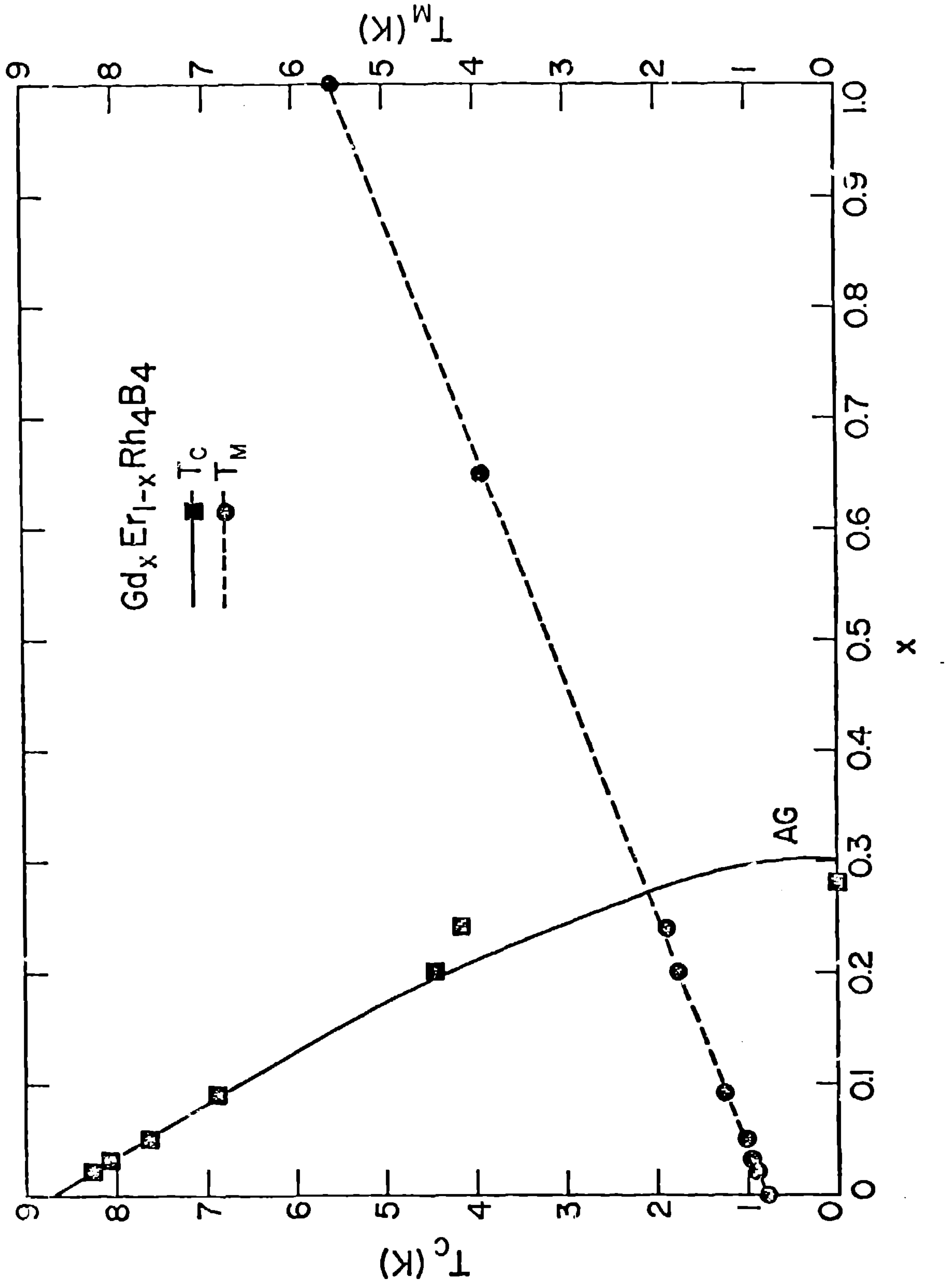



Fig. 1



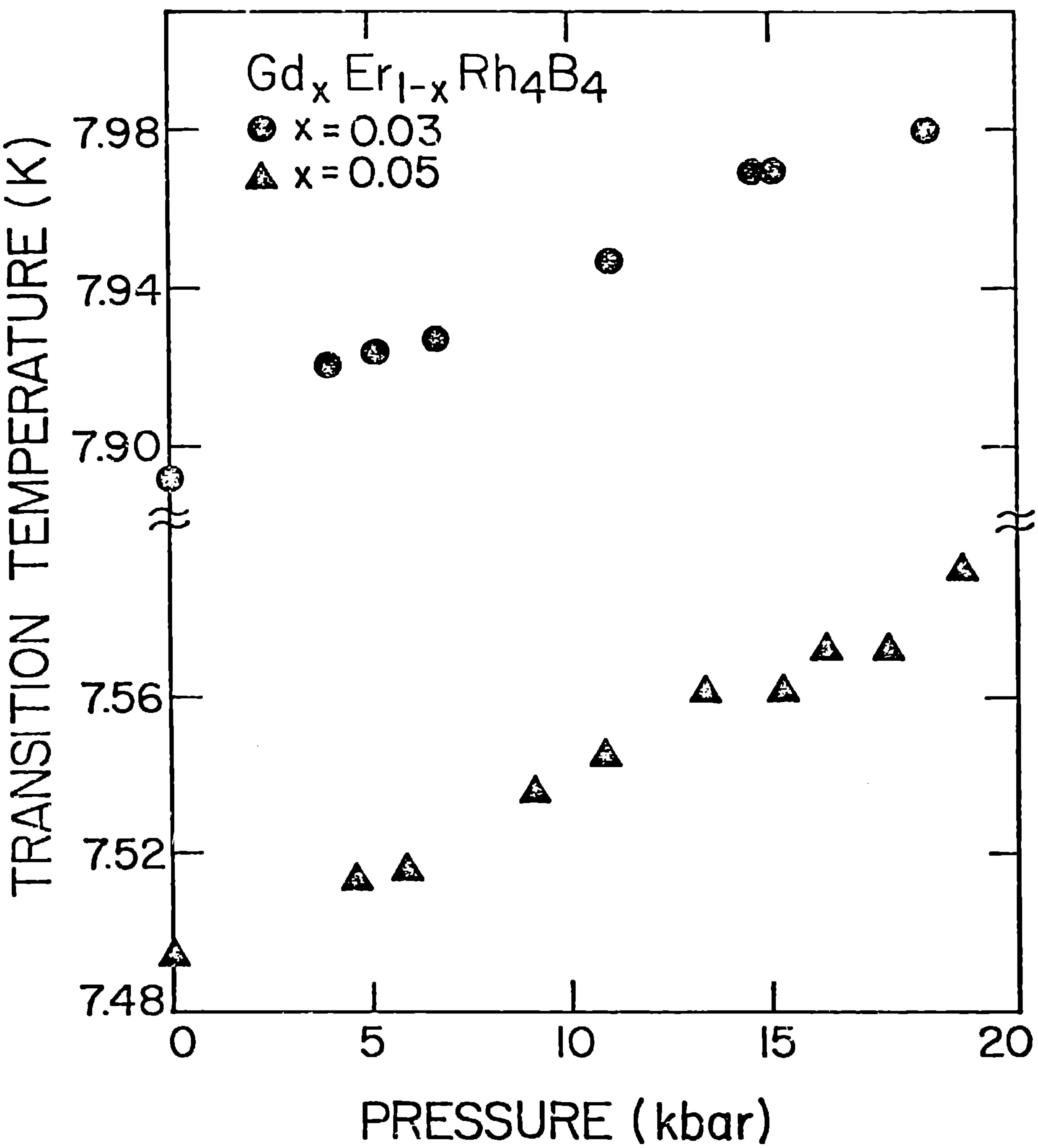
Gd$_x$ Er$_{1-x}$ Rh$_4$ B$_4$
x = 0.02
0.03
0.00
0.05
0.09
0.20
0.24
H$_{c2}$ (kOe)
T (K)
0
1
2
3
4
5
6
7
8
9


Fig. 2



Gd$_x$Er$_{1-x}$Rh$_4$B$_4$
T$_C$
T$_M$
AG
x
T$_c$ (K)
T$_M$ (K)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
1
2
3
4
5
6
7
8
9


Fig. 3



$Gd_x Er_{1-x} Rh_4 B_4$
x = 0.03
x = 0.05
TRANSITION TEMPERATURE (K)
7.98
7.94
7.90
7.56
7.52
7.48
0
5
10
15
20
PRESSURE (kbar)


Fig. 4