Shenoy, Dunlap, Fradin, eds. TERNARY SUPERCONDUCTORS

PRESSURE DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE OF $(Th_{1-x}Y_x)Rh_4B_4$

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The pressure dependence of the superconducting transition temperatures, T_c's, of fourteen samples in the pseudoternary system $(Th_{1-x}Y_x)Rh_4B_4$ are reported for hydrostatic pressures up to 21 kbar. The Y rich samples show an enhancement of T_c with applied pressure, whereas for the Th rich compounds T_c is depressed by pressure. A broad plateau in dT_c/dp as a function of x is observed for nearly equiatomic ($0.4 \leqslant x \leqslant 0.80$) compositions. The non-linear behavior of T_c as a function of pressure for the Y rich samples ($x>0.80$) is discussed with reference to prior measurements on YRh_4B_4. Observation of this non-linearity may be related to the purity of the Y source material or the presence of a pressure-induced phase transformation.

INTRODUCTION

Superconductivity and magnetic order in the class of ternary compounds MRh_4B_4, (M=Nd,Sm,Gd,Tb,Dy,Ho,Er,Tm,Lu,Th,Y), was first reported by Matthias and co-workers in 1977 [1,2]. These materials have received considerable attention since that time due to the variety of electronic and magnetic properties they exhibit [3]. The first pressure measurements on these materials indicated that for the superconducting rare earth compounds, the third element played a crucial role in determining the pressure dependence of the transition temperature (T_c) [4]. That investigation found that dT_c/dp increased with decreasing size of the rare earth element. In the same study the unique non-linear behavior of T_c under pressure for $LuRh_4B_4$ was reported. This was attributed to a speculated pressure induced phase change. In order to better understand the role of the third element in determining the electronic properties and particularly dT_c/dp of these compounds, the pseudoternary system $(Th_{1-x}Y_x)Rh_4B_4$ was chosen for study. This system exhibits no magnetic order and covers a wide range of superconducting transition temperatures. Moreover T_c is depressed by applied pressure for $ThRh_4B_4$ and enhanced for YRh_4B_4, even though Th and Y have similar metallic radii.

EXPERIMENTAL DETAIL

All samples in this investigation were prepared by arc melting stoichiometric mixtures of the elements in a Zr-gettered argon atmosphere. Powder x-ray diffraction analysis indicates these as cast samples form the primitive tetragonal $CeCo_4B_4$-type structure [5] with less than ten percent of an unidentified impurity phase. The superconducting transition temperatures were determined using a low frequency inductance technique. Hydrostatic pressures up to 21 kbar were generated at room temperature using a 1:1 mixture of iso-amyl alcohol and n-pentane as a pressure transmission medium. A hardened Be-Cu clamp maintained the pressure at low temperatures. The applied pressure was determined at low temperatures using a superconducting manometer [6]. The transition of each sample was very sharp and remained sharp under pressure, varying from 25 mK wide for YRh_4B_4 to a maximum of 250 mK wide for some of the intermediate composition samples. Pressure data were obtained in a series of measurements consisting of an initial determination of $T_c(0)$ followed by measurements at increasingly higher pressures until a maximum pressure in excess of 20 kbar was attained. The pressure was then released and the series repeated at different pressures. In each case the zero pressure T_c was well replicated and in no case was any hysteresis observed.

RESULTS AND DISCUSSION

The zero pressure T_c's for these samples are presented in Fig. 1 as a function of Y concentration. T_c increases in a smooth, monotonic fashion from 4.41 K for $ThRh_4B_4$ to a maximum of 10.54 K for YRh_4B_4, an increase of greater than 6 K. This large increase is consistent with recent band structure calculations which place the Fermi level at a narrow peak in the density of states for $HoRh_4B_4$ and $ErRh_4B_4$ [7,8]. The lattice parameters, c/a values and unit cell volumes vary linearly with x, obeying Vegard's law and are shown in Fig. 2. As for all other members of this class, c/a is always less than $\sqrt{2}$,

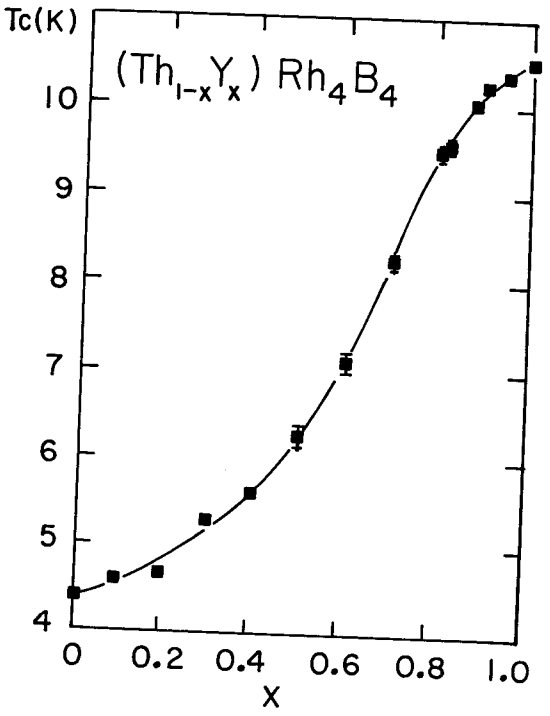

Fig. 1. Superconducting transition temperatures for the system $(Th_{1-x}Y_x)Rh_4B_4$ plotted versus the Y concentration. Vertical error bars indicate the width of the transition into the superconducting state.

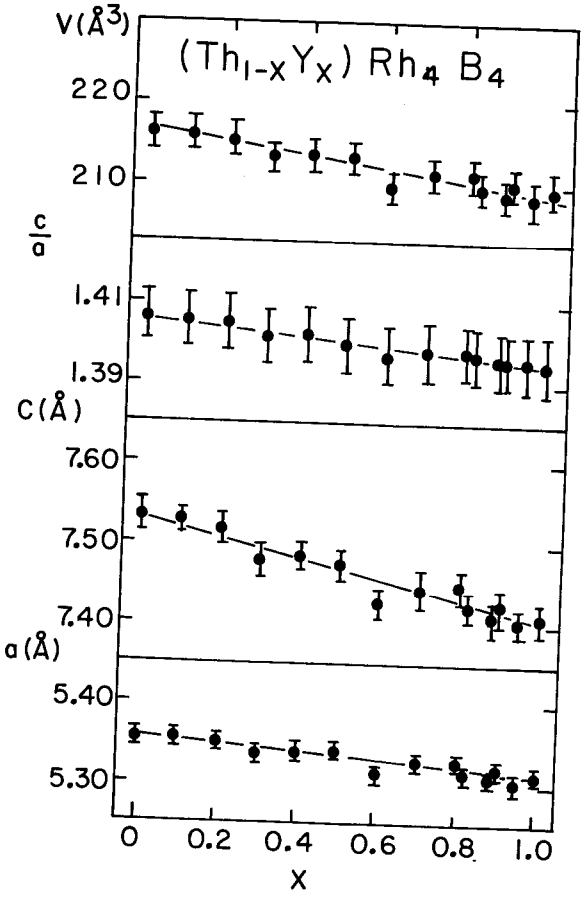

Fig. 2. Lattice parameters, c/a values and unit cell volumes for the system $(Th_{1-x}Y_x)Rh_4B_4$ as a function of Y concentration.

The value at which the third element would comprise a face-centered cubic sublattice. The contraction of the unit cell volume, $\Delta V/V$, upon complete substitution of Y for Th is 2.5%. To estimate the unit cell volume contraction due to pressure we made a reasonable compressibility estimate of 10^{-3} kbar^{-1}. A maximum pressure change of 20 kbar then yields a 2% decrease in unit cell volume which is the same order of magnitude as the change due to total Y substitution for Th. The maximum change observed in T_c due to pressure was +0.12 K, an order of magnitude smaller than the 6.1 K change due to the substitution of trivalent Y for tetravalent Th. This indicates that the dominant influence on T_c is the electronic nature of the third element rather than it's effect on the unit cell volume. Additionally, the mass of the third element does not appear to be an important factor in determining T since the heaviest rare earth which forms the structure (Lu) also has the highest T_c. This is exactly opposite to the behavior of $T_c(0)$ in the $(Th_{1-x}Y_x)Rh_4B_4$ system.

An initial hydrostatic pressure study indicated that T_c was a linear function of pressure for YRh_4B_4. The distinctly non-linear behavior shown in Fig. 3 is in sharp contrast to this earlier work. We attribute the observation of the non-linearity to the improved quality of the samples as reflected in much narrower transitions into the superconducting state. The transition width for YRh_4B_4 is 25 mK compared to the 110 mK in the prior work. The present samples were also synthesized from higher purity Y [9]. The development of the non-linear feature can be seen in Fig. 3 as the Y concentration is increased. The feature is completely absent in the x=0.80 sample and becomes more evident with increasing x until it is quite distinct in the YRh_4B_4 sample. The x=0.82 sample data can be fitted well by a single straight line, but a break in slope has been shown to allow comparison with higher x-valued samples. All six samples in the figure show a nearly zero pressure dependence of T_c below 7

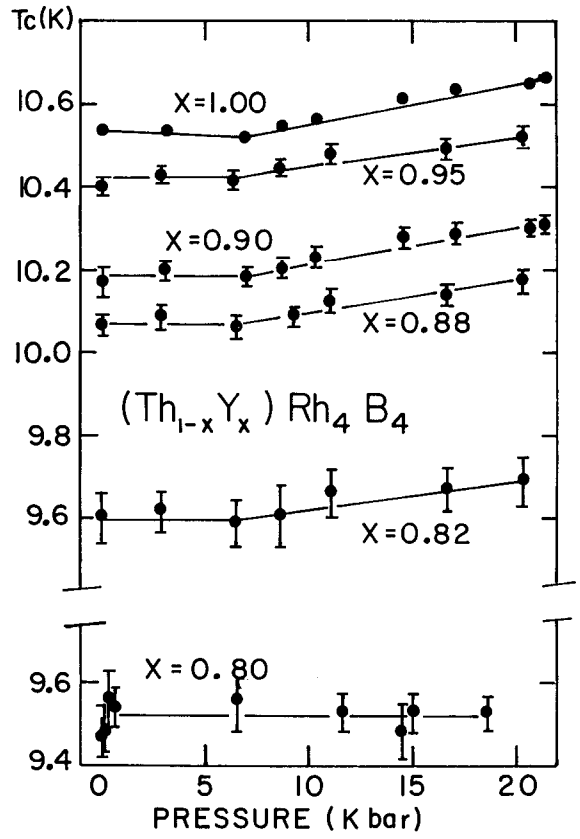

Fig. 3. T_c versus hydrostatic pressure for six samples with high Y concentration in the system $(Th_{1-x}Y_x)Rh_4B_4$. Vertical error bars indicate the width of the transition into the superconducting state. Zero pressure data points represent more than one measurement.

kbar. For $x \leq 0.80$ all the samples show a linear dependence for T_c on pressure and were fitted by the method of least squares. These results are presented in Fig. 4 where both the high and low pressure slopes are included for the high Y concentration samples.

Although $T_c(0)$ depends strongly on both the choice of rare earth and transition metal (Rh, Ir), [10,11] the pressure dependence, dT_c/dp, appears to depend most strongly on the specific rare earth. The complex behavior of dT_c/dp as a function of x was, in this context, unexpected, particularly the nonlinearity of $T_c(p)$ for YRh_4B_4. For the composition range $0.00 \leq x \leq 0.40$ dT_c/dp shows a linear increase, much as in the $Th_{1-x}Y_x$ elemental system [12]. The reappearance of a non-zero pressure dependence at high pressure for the Y rich samples ($x \geq 0.82$) may be a continuation of this trend. The transition temperature shows no pressure dependence for

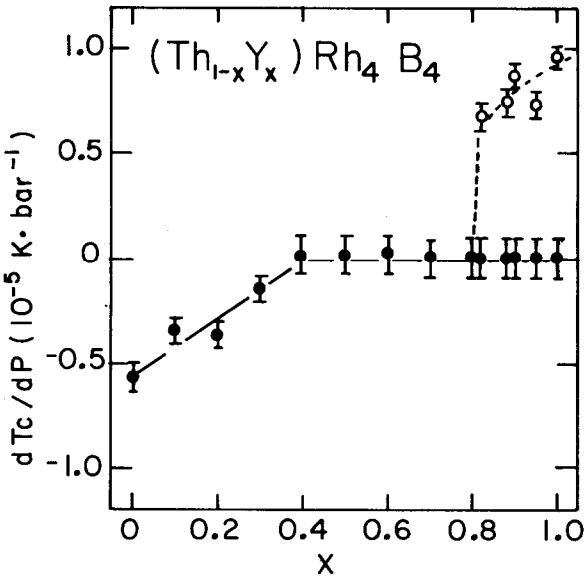

Fig. 4. Pressure derivatives of the superconducting transition temperatures versus Y concentration for the system $(Th_{1-x}Y_x)Rh_4B_4$. Open circles (○) indicate derivatives evaluated at high pressure (see text for details).

samples in the range $0.40 \leq x \leq 0.80$ at all pressures measured. Additionally compounds with $0.80 \leq x \leq 1.00$ also have horizontal T_c vs. p curves for pressures below 7 kbar. We note that this insensitivity of T_c to pressure exists over a large range of unit cell volume, $\Delta V/V \approx 2\%$.

The discrete change in dT_c/dp at 7 kbar for five high Y-concentration samples and the wide range of concentration where $dT_c/dp \approx 0$ are not readily understood. Since increasing x contracts the lattice and is in this sense equivalent to applying pressure, we see this insensitivity of T_c to pressure at low pressure for the high Y concentration samples as just a continuation of the effect seen for the $0.40 \leq x \leq 0.80$ samples. The similarity of dT_c/dp for $p \geq 7$ kbar in all Y rich samples may be evidence that the same pressure-induced change occurs. This change "locks in" more strongly for higher Y-concentrations, thus resulting in a more pronounced kink for samples with higher x values. We note, however, the critical pressure, p_c, for the onset of this pressure-induced phase transformation is not concentration dependent and remains constant at about 7 kbar. The complete lack of pressure dependence on T_c over the range $0.40 \leq x \leq 0.80$ is surprising because of the large composition range involved. This could be due to a gradual increase in the bulk modulus over the range $0.00 \leq x \leq 0.40$ resulting in a stiffer lattice. This stiffness is maintained at all compositions $x \geq 0.40$ for pressure below p_c and at

all pressures for compositions $0.40 \leqslant x \leqslant 0.80$, and is only relieved by a pressure-induced phase change in the Y rich samples. A final consideration is the role of the preparation procedure and purity of constituent elements in affecting dT_c/dp.

Due to the sharpness of the transitions, the reproducibility of the data over numerous cycles in pressure and the internal consistency of the break in slope in $T_c(p)$ for high x-value samples, we feel these results are intrinsic to this sytem of compounds. Future work includes low temperature x-rays to search for possible lattice distortions indicative of a phase change. No such distortions were observed in $LuRh_4B_4$, previously considered unique in it's non-linear T_c dependence on pressure. Perhaps even more crucial to understanding the break in slope at p_c would be x-ray diffraction data on YRh_4B_4 and $LuRh_4B_4$ at pressures above p_c. Density measurements are planned to determine the vacancy population, if any, as a factor relevent to the compressibility and perhaps controllable by preparation techniques.

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