

## Doping and high-pressure study on $\text{Lu}(\text{Ni}_{1-x}\text{A}_x)\text{BC}$ with $\text{A}=\text{Cu}$ and $\text{V}$

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(Received 18 December 1995)

The effects of doping and pressure on the superconducting transition temperature ( $T_c$ ) of  $\text{Lu}(\text{Ni}_{1-x}\text{A}_x)\text{BC}$  with  $\text{A}=\text{Cu}$  and  $\text{V}$  have been investigated.  $T_c$  was found to increase with Cu doping, but decrease with V doping, and pressure was observed to suppress all samples, doped or undoped, examined at a constant rate of  $\sim -0.17 \pm 0.3$  K/GPa. The observations are not consistent with the predicted Fermi surface of  $\text{LuNiBC}$  residing at a density-of-states peak, and the pressure effect on  $T_c$  cannot be understood in terms of shift in the Fermi surface alone. [S0163-1829(96)02118-2]

The discovery of superconductivity in a new family of boro-carbide intermetallic compounds,  $L\text{-Ni-B-C}$ , has generated considerable interests recently,<sup>1</sup> where  $L$  is Y or lanthanide elements (Ho, Er, Tm, Tb, and Lu).  $T_c$  was found to be 16.6 K for the quaternary compound  $\text{LuNi}_2\text{B}_2\text{C}$ ,<sup>1</sup> which may be viewed as a stacking of  $\text{Ni}_2\text{B}_2$  and  $\text{LuC}$  layers.<sup>2</sup> A closely related compound  $\text{LuNiBC}$ , which can be derived from  $\text{LuNi}_2\text{B}_2\text{C}$  by inserting another  $\text{LuC}$  layer between two adjacent  $\text{Ni}_2\text{B}_2$  blocks, is also a superconductor.<sup>3</sup> However, its  $T_c$  is only 2.9 K (Ref. 3) despite the fact that the corresponding bond distances and bond angles are almost the same in these two compounds. The difference in  $T_c$  has been interpreted based on the different densities of states  $N(E)$  at the Fermi level  $E_F$  for the two compounds.<sup>4-6</sup> According to band-structure calculations,<sup>4-6</sup> these two compounds have a similar general feature in  $N(E)$ : most states located a few eV below or above the Fermi level ( $E_F$ ), except a few bands within 0.5 eV around  $E_F$ , resulting in an  $N(E)$  minimum just below an  $N(E)$  peak in this energy region. However, the subtle structural difference between the two compounds causes the  $E_F$  of  $\text{LuNi}_2\text{B}_2\text{C}$  to reside at the  $N(E)$  peak whereas the  $E_F$  of  $\text{LuNiBC}$  to situate at the  $N(E)$  minimum just below the corresponding  $\text{LuNi}_2\text{B}_2\text{C}$  peak. In the framework of BCS theory, the higher  $T_c$  of  $\text{LuNi}_2\text{B}_2\text{C}$  can therefore be understood in terms of its higher  $N(E_F) \sim 4.8$  states/(eV cell). The low  $T_c$  of  $\text{LuNiBC}$  is then ascribed to the low  $N(E_F)$  of the compound. It was suggested that the  $T_c$  of  $\text{LuNiBC}$  could be substantially enhanced by raising  $E_F$  (by about 1 electron/cell) through substitutional doping, assuming that  $N(E_F)$  is the dominant change during the substitution.

In order to test these propositions, we measured the effects of both doping and pressure on the  $T_c$  of  $\text{LuNiBC}$ .  $\text{Cu}(3d^{10}4s^1)$  and  $\text{V}(3d^34s^2)$ , which are on opposite sides of Ni ( $3d^84s^2$ ) in the periodic table, were used to increase and decrease the conduction electrons of  $\text{LuNiBC}$  in our doping study. According to the band calculations,  $T_c$  should increase in both cases if the Fermi level of  $\text{LuNiBC}$  lies at an  $N(E)$  minimum, in the rigid-band approximation. For the same reason, pressure is expected to suppress the  $T_c$  of V-doped  $\text{LuNiBC}$  and enhance the  $T_c$  of Cu-doped samples, provided that the pressure effect is dominated by the rise of conduction electron density as in most cases. As to the undoped  $\text{LuNiBC}$ ,  $T_c$  should increase with pressure due to a pressure-

induced  $N(E_F)$  increase associated with either a band broadening or an  $E_F$  shift. Unfortunately, contrary to above predictions, we observed that the  $T_c$  of  $\text{LuNiBC}$  increases with Cu doping, but decreases with V doping, and that pressure reduces the  $T_c$  at a rate of  $\sim -0.17 \pm 0.3$  K/GPa for all doped and undoped samples investigated. The observations suggest that the Fermi level may situate away from the  $N(E)$  minimum, instead of at the  $N(E)$  minimum as predicted. The negative pressure effect on  $T_c$  observed in all samples examined shows that pressure influences not just the electron concentration, but also other factors, such as the electron-phonon coupling.

All samples in this investigation were prepared from high-purity elements (Lu 99.9%, Ni 99.8%, B 99.999%, C 99.9%, Cu 99.9%, and V 99.5%) by arc-melting stoichiometric mixtures in a water-cooled Cu sheath under an argon atmosphere. The buttons were turned over at least 4 times between melts to promote homogeneity. The total weight loss due to arc melting was less than 1%. X-ray powder diffraction was performed by a Rigaku D-MAX III diffractometer. The  $T_c$  was measured using the standard four-lead method on bar-shaped samples cut from arc-melted buttons. The hydrostatic pressure environment for the electrical measurements was generated by a modified self-clamp technique,<sup>7</sup> using 3M Fluorinert as the pressure medium. The applied pressure was changed at room temperature after each run. A Pb manometer situated next to the sample was used to determine the pressure and a Ge thermometer the temperature.

The phase purity of the samples was checked by x-ray powder diffraction. Layered  $\text{LuNiBC}$  was the major phase ( $>95\%$ ) in the undoped samples [Fig. 1(a)]. Both the  $\text{Lu}(\text{Ni}_{1-x}\text{Cu}_x)\text{BC}$  and  $\text{Lu}(\text{Ni}_{1-x}\text{V}_x)\text{BC}$  samples were nearly single phase with  $x < 0.25$  [Fig. 1(b)]. With  $x \geq 0.25$ , excessive impurities appeared, suggesting the solubility limit of Cu/V in  $\text{LuNiBC}$  was  $\sim 0.25$ .

Typical temperature dependences of the resistivity  $\rho$  are shown in Fig. 2 for  $\text{Lu-Ni-B-C}$ ,  $\text{Lu}(\text{Ni}_{0.8}\text{V}_{0.2})\text{BC}$ , and  $\text{Lu}(\text{Ni}_{0.8}\text{Cu}_{0.2})\text{BC}$ , displaying a superconducting transition with a width varying between 0.2 and 0.4 K. The corresponding onset transition temperatures ( $T_c$ ) are 2.96, 2.60, and 3.38 K, respectively. Cu doping results in an enhancement of  $T_c$  at a relative rate of  $d \ln T_c / dx \sim 0.5$ , while V doping leads to a  $T_c$  decrease at a rate of  $d \ln T_c / dx \sim -0.5$ , as shown in Fig. 3. Since the substitutional replacement of

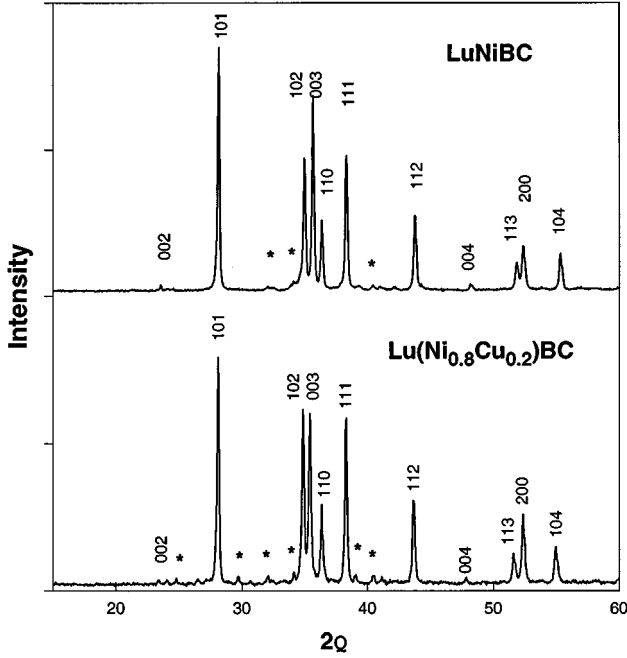


FIG. 1. X-ray diffraction patterns of powder samples: (a)  $\text{LuNiBC}$  and (b)  $\text{Lu}(\text{Ni}_{0.8}\text{Cu}_{0.2})\text{BC}$ .

Ni by Cu increases the conducting electron concentration and upshifts  $E_F$  toward the  $N(E)$  peak, the enhanced  $T_c$  of  $\text{LuNiBC}$  by Cu doping is consistent with the band calculations within the framework of the rigid-band model. Unfortunately, V doping, which is supposed to down shift  $E_F$  away from the  $N(E)$  minimum and suppress the  $T_c$ , is in contrast to predictions. The results imply that the  $E_F$  of  $\text{LuNiBC}$  may be located between the  $N(E)$  minimum and the  $N(E)$  peak with a  $dN(E)/dE > 0$ .

To gain further insight into the above observations, the normal-state  $\rho(T)$ 's of these samples were compared (Fig. 2, inset). The resistivity of all our samples depends on  $T$  linearly between 120 and 300 K with the similar relative slope  $(d\rho/dT)/\rho(300\text{ K}) \sim 0.0018 \pm 0.0002/\text{K}$ , independent of doping. Therefore, one might tentatively attribute the doping ef-

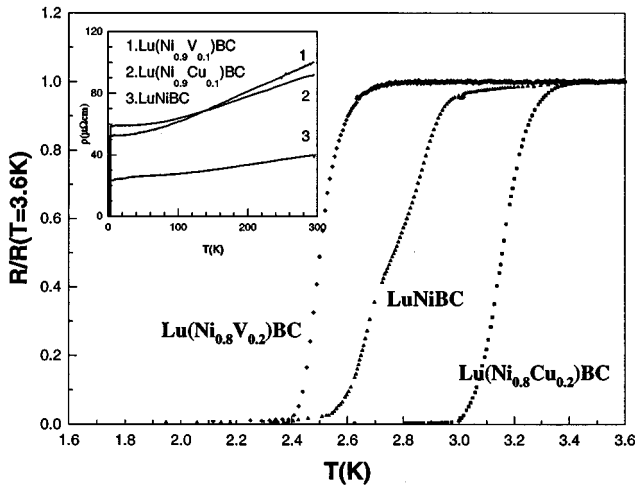


FIG. 2.  $T$  dependence of  $\rho$  of  $\text{LuNiBC}$ ,  $\text{Lu}(\text{Ni}_{0.8}\text{Cu}_{0.2})\text{BC}$ , and  $\text{Lu}(\text{Ni}_{0.8}\text{V}_{0.2})\text{BC}$  at ambient pressure.

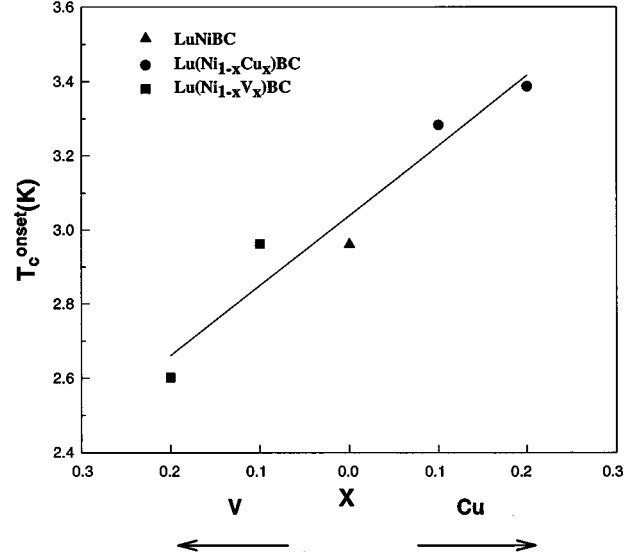


FIG. 3.  $T_c$  in  $\text{Lu}(\text{Ni}_{1-x}\text{A}_x)\text{BC}$  with  $A=\text{Cu}$  and  $\text{V}$  and  $x=0.0$ ,  $0.1$ , and  $0.2$ .

fect of  $\rho$  to the change of  $N(E)$ , by assuming  $\rho \propto 1/N(E_F)$ . The observed  $\rho$  nearly doubled with either  $0.1$  Cu or  $0.1$  V doping (Fig. 2, inset). The drastic increase of  $\rho$  with both Cu and V doping combined with the observed  $T_c$  decreases with V doping cannot simply reconcile with either the prediction that the  $E_F$  of  $\text{LuNiBC}$  locates at a local  $N(E)$  valley by band calculations or even the conjecture that  $E_F$  may reside on the side of the  $N(E)$  valley with  $dN(E)/dE > 0$  implied by the doping effect. However, it should be noted that  $\rho$  is rather sensitive to various scattering processes and the assumption of  $\rho \propto 1/N(E_F)$  should be taken with caution.

The pressure effects on  $T_c$  and  $\rho$  of the undoped and doped samples have been measured up to  $1.5$  GPa. The resistive superconducting transition shifted parallel downward under pressure for all the samples as exemplified by  $\text{Lu}(\text{Ni}_{0.8}\text{Cu}_{0.2})\text{BC}$  in Fig. 4.  $dT_c/dP$ 's are negative and have roughly the same value of  $-0.17 \pm 0.3$  K/GPa for all the undoped, Cu-doped, and V-doped  $\text{LuNiBC}$ , as summarized in Fig. 5. Pressure usually can be regarded as either to

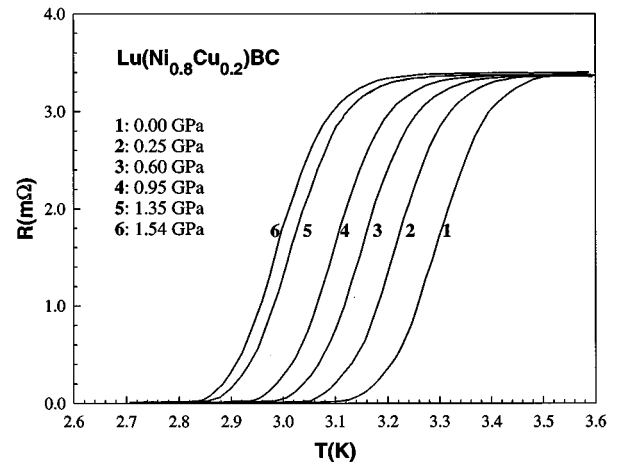


FIG. 4.  $T$  dependence of  $\rho$  in  $\text{Lu}(\text{Ni}_{0.8}\text{Cu}_{0.2})\text{BC}$  at various pressures  $\leq 1.5$  GPa.

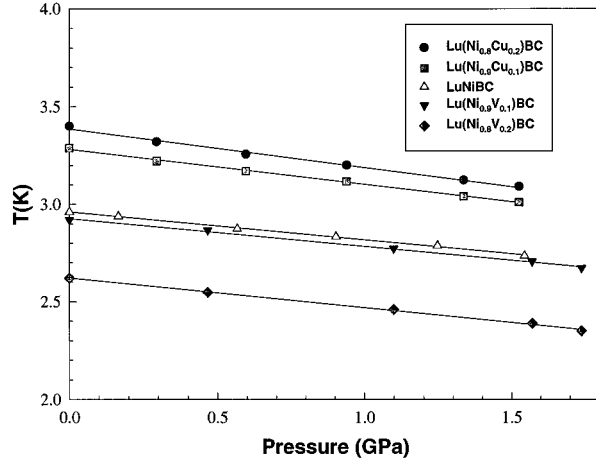


FIG. 5. Dependence of the superconducting  $T_c$  on hydrostatic pressure for  $\text{Lu}(\text{Ni}_{1-x}\text{A}_x)\text{BC}$  with  $\text{A}=\text{Cu}$  and  $\text{V}$  with  $x=0.0$ ,  $0.1$ , and  $0.2$ .

shift the  $E_F$  upward or broaden the bands slightly in the rigid-band model. In either case,  $dT_c/dP$  should be positive for undoped  $\text{LuNiBC}$  if the  $E_F$  lies at a local  $N(E)$  minimum and  $T_c$  is dominated by  $N(E_F)$ . The observed negative  $dT_c/dP$  of  $\text{LuNiBC}$  was not what was expected. Similarly, the  $dT_c/dP$  of  $\text{Lu}(\text{Ni}_{1-x}\text{V}_x)\text{BC}$  and that of  $\text{Lu}(\text{Ni}_{1-x}\text{Cu}_x)\text{BC}$  should either have different signs, if the  $E_F$  shift dominates the pressure effect, or be smaller than the  $dT_c/dP$  of  $\text{LuNiBC}$ , if band broadening is the main factor. The observed nearly constant negative pressure effect suggests that the real situation may be rather complicated and the change of  $T_c$  under pressure may not be interpreted in terms of an  $N(E_F)$  change alone.

Figure 6 shows that the normal-state resistivity decreases with pressure for the undoped  $\text{LuNiBC}$ , but is essentially

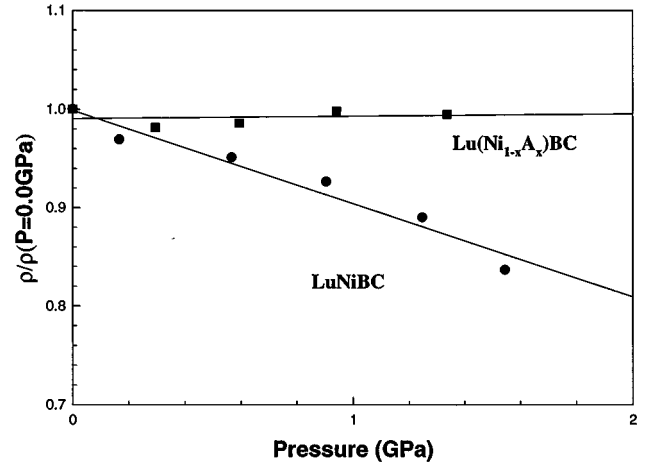


FIG. 6. Dependence of the normal-state  $\rho$  on pressure for  $\text{Lu}(\text{Ni}_{1-x}\text{A}_x)\text{BC}$ .

unaffected by pressure for all the doped samples. This again demonstrates the complication of the pressure effect.

In conclusion,  $T_c$  and  $\rho(T)$  have been measured in undoped, Cu-doped, and V-doped  $\text{LuNiBC}$  at ambient and hydrostatic pressures.  $T_c$  increases with Cu doping, but decreases with V doping. Under pressure, a nearly constant  $dT_c/dP$  was observed for all examined compounds. Our results are not consistent with the prediction that the  $E_F$  of  $\text{LuNiBC}$  lies at a local  $N(E)$  minimum and suggests that the pressure effect cannot be interpreted in terms of the pressure-induced  $N(E_F)$  change alone in these compounds.

This work is supported in part by NSF Grant No. DMR 95-00625, EPRI Grant No. RP-8066-04, the State of Texas through the Texas Center for Superconductivity at the University of Houston, and the T.L.L. Temple Foundation.

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