Superconductivity in $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$

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We have studied $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$ at ambient and high pressures. Superconductivity was discovered in $(LuC)_2(Ni_2B_2)$ at 2.9 K. Pressure was found to suppress both the electrical resistivity and the superconducting transition temperature rapidly for $(LuC)_2(Ni_2B_2)$ but only slightly for $(LuC)(Ni_2B_2)$, in spite of their similar chemical-bonding behavior. The observations can be understood in terms of the smaller density of states at the Fermi surface and the greater pressure-induced band broadening of $(LuC)_2(Ni_2B_2)$ than $(LuC)(Ni_2B_2)$.

I. INTRODUCTION

Recently, Cava *et al.*[1] discovered superconductivity in a new family of intermetallic compounds, $RNi_2B_2C=(RC)(Ni_2B_2)$, where R =Lu, Y, Tm, Er, and Ho, with a transition temperature (T_c) varying from 17 to 8 K. Later, Eisaki *et al.*[2] observed that the T_c scales approximately with the de Gennes factor, implying that there exists a non-negligible coupling between the rare-earth magnetic moments and the conduction electrons. Siegrist *et al.*[3] found that $(RC)(Ni_2B_2)$ displays a tetragonal body-centered layerlike structure with a $I4/mmm$ symmetry. $(RC)(NI_2B_2)$ may thus be considered as alternate stackings of the NaCl-type (RC) and the inverse PbO-type (Ni_2B_2) layers. The unit-cell volume of RNi_2B_2C increases with the ionic radius of R. Superconductivity appears to be confined to those with R smaller than Tb. It was further suggested[3] that the insertion of more (RC) and/or (Ni_2B_2) layers gives rise to the homologous series $(RC)_m(Ni_2B_2)_n$ with n and $m=1,2,\ldots$. Indeed, $(LuC)_2(Ni_2B_2)$ was found to exist in a tetragonal structure with a $P4/nmm$ symmetry. However, $(LuC)_2(Ni_2B_2)$ was reported[3] to be not superconducting.

Despite the scaling of the T_C and the de Gennes factor of RNi_2B_2C, $LaNi_2B_2C$ with the nonmagnetic La is not superconducting. The clustering of the superconducting RNi_2B_2C to those with a small R's suggests that interatomic and interlayer spacing may also play a role in this interesting compound family. Although coupling between (Ni_2B_2) layers is strong as evidenced by the short B—C bonds[3] and the small anisotropy in the magnetic properties of a similar compound Y-Pd-B-C,[4] the layered structure of $(RC)_m(Ni_2B_2)_n$ is a reminiscence of the layered cuprates, e.g., $(TlO)_m(BaO)_2(Ca_{1-1n}CuO_2)_n$ $=Tl_mBa_2Ca_{n-1}Cu_nO_{2n+m+2}$ with $m=1$ or 2, $n=1,2,\ldots$. For the cuprates, the T_c is higher for $m=2$ than for $m=1$.[5] The reported absence of superconductivity in $(LuC)_2(Ni_2B_2)$ to a certain extent is unexpected in view of the high $T_c=17$ K for $(LuC)(Ni_2B_2)$.

In this paper, we report the observation of superconductivity in $(LuC)_2(Ni_2B_2)$ with $T_c=2.9$ K. In spite of the similar chemical bonding behavior[3] in $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$, the reduced pressure effect on T_c, i.e., $(d\ln T_c/dP)$ is $\sim -4.7\times10^{-2}$ GPa^{-1} for the former, about 16 times greater than that for the latter. We attribute these observations to the possible lower electron density of states and the greater band broadening of $(LuC)_2(Ni_2B_2)$ under pressure when compared to those of $(LuC)(Ni_2B_2)$. This is in qualitative agreement with the electrical transport measurements on the compounds.

II. EXPERIMENTAL

The $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$ samples examined were prepared by the arc-melt technique. The starting materials were Alfa Lu chips (99.9%), Alfa Ni wires (99.8%), Pither Industries B grains (99.999%), and Alfa

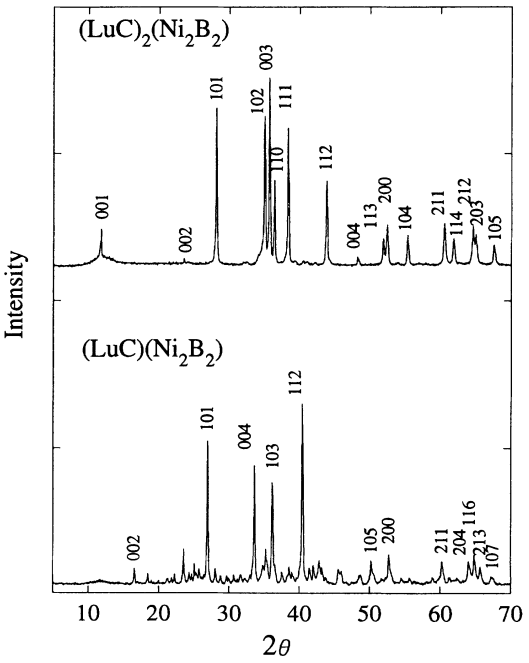

FIG. 1. The x-ray-diffraction patterns of $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$.

C wafers (99.9%). Stoichiometric amounts of the starting materials were arc melted in a water-cooled Cu hearth in an Ar atmosphere at least four times. The buttons were turned over between melts to enhance homogeneity. The overall loss in weight of the sample due to arc melting was less than 1%.

Bar-shaped samples were cut from the arc-melted buttons for electrical and magnetic measurements. The resistivity was determined by the standard four-lead method, the magnetic susceptibility by a Quantum Design superconducting quantum interference device (SQUID) magnetometer and the structure by a Rigaku D-MAX III powder diffractometer. The hydrostatic-pressure environment for the electrical measurements was generated by the self-clamp technique,[6] using 3M Fluorinert as the fluid pressure medium. A superconducting Pb manometer situated next to the sample was used for the pressure determination and a Ge thermometer for the temperature.

III. RESULTS AND DISCUSSION

The x-ray powder-diffraction patterns of the $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$ samples are shown in Fig. 1. The purity of the $(LuC)_2(Ni_2B_2)$ sample is greater than 95% and that of the $(LuC)(Ni_2B_2)$ is only about 80 to 90% with a small amount of unknown impurities. The lattice parameters are $a=3.492$ and 3.467 Å and $c=7.552$ and 10.633 Å, respectively for $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$, in good agreement with the previously published results.[3] The observed intensities of the diffraction lines are compared with the calculated ones based on the atomic positions given by Siegrist *et al.*,[3] as shown in Table I. For later discussions, the layerlike atomic arrangements are shown for the two compounds in Fig. 2.

The resistivity ρ of the two compounds is displayed in Fig. 3 as a function of temperature. $(LuC)_2(Ni_2B_2)$ is clearly superconducting with $T_c \sim 2.9$ K, in contrast to a

TABLE I. Comparison between observed diffraction-line intensities and calculated intensities based on the atomic positions given in Ref. 3.

$(LuC)_2(Ni_2B_2)$ Space-group $P4/nm$ Tetragonal	$a=3.492$ Å		$c=7.552$ Å	
hkl	*d* (calculated)	*d* (observed)	I/I_0 (calculated)	I/I_0 (observed)
001	7.553	7.526	7	17
002	3.776	3.775	10	4
101	3.170	3.169	100	84
102	2.564	2.565	80	71
003	2.518	2.516	47	100
110	2.470	2.470	27	44
111	2.347	2.348	65	62
112	2.067	2.065	40	45
004	1.888	1.883	2	4
113	1.763	1.762	16	15
200	1.746	1.745	35	23
104	1.661	1.660	18	17
211	1.530	1.530	27	20
114	1.500	1.499	21	14
212	1.443	1.443	29	18
203	1.435	1.433	32	13
105	1.386	1.386	11	9
$(LuC)(Ni_2B_2)$ Space-group $I4/mmm$ Tetragonal	$a=3.467$ Å		$c=10.633$ Å	
hkl	*d* (calculated)	*d* (observed)	I/I_0 (calculated)	I/I_0 (observed)
002	5.316	5.336	6	10
101	3.294	3.299	66	79
004	2.658	2.661	38	65
103	2.477	2.482	45	57
112	2.225	2.228	100	100
105	1.812	1.814	17	15
200	1.732	1.732	25	16
211	1.533	1.533	16	11
204	1.451	1.452	23	14
116	1.436	1.438	25	17
213	1.419	1.419	17	9
107	1.391	1.392	6	5

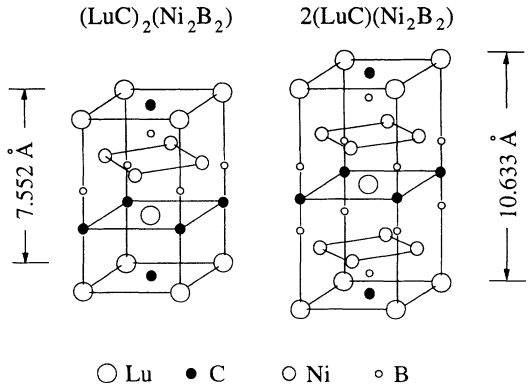

FIG. 2. The layered structures of $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$.

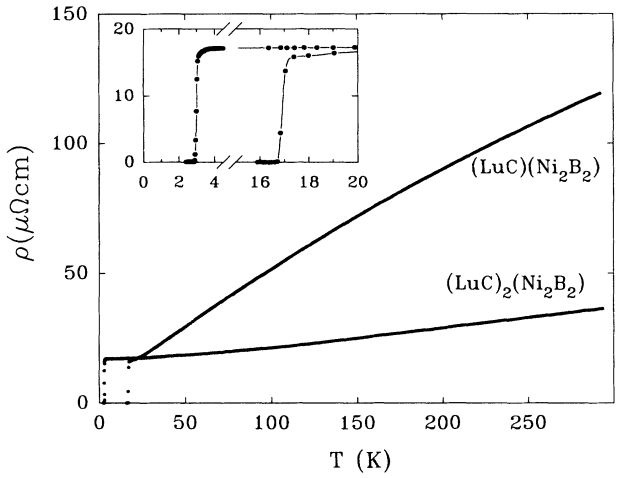

FIG. 3. The temperature dependence of ρ of $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$. Inset: expanded T scales.

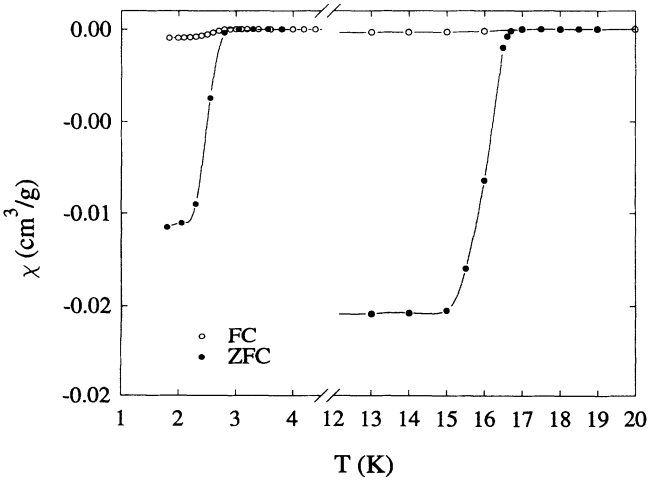

FIG. 4. The temperature dependence of χ of $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$.

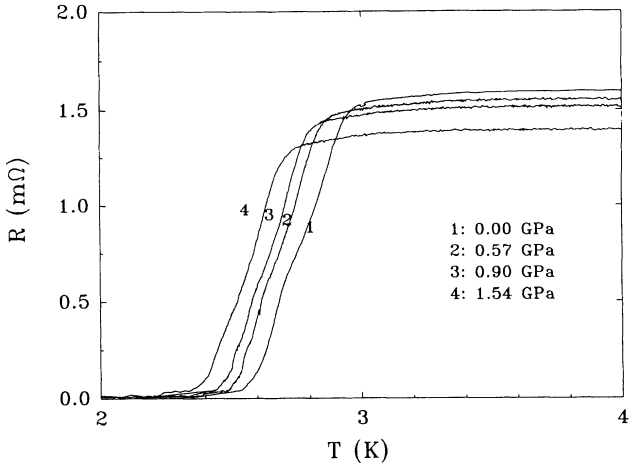

FIG. 5. The superconducting transitions of $(LuC)_2(Ni_2B_2)$ under various pressures.

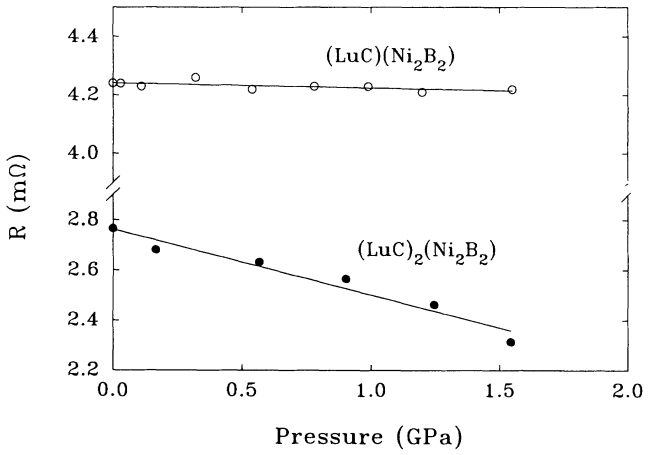

FIG. 6. The pressure dependence of ρ at 290 K for $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$.

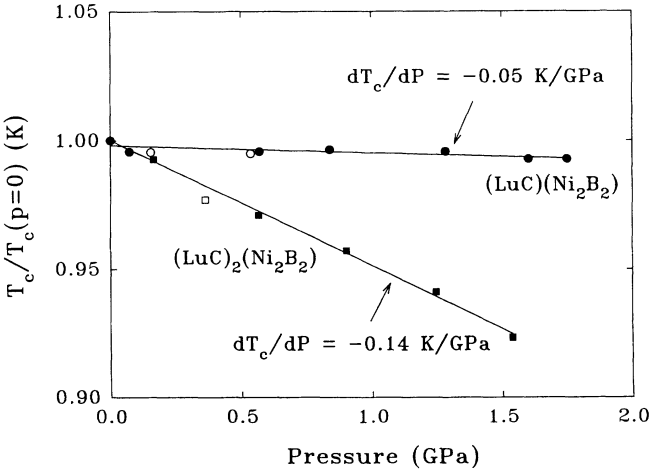

FIG. 7. The normalized pressure effect on T_c of $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$. Unfilled symbols represent data obtained upon pressure reduction.

previous report.[3] The T_c of $(LuC)(Ni_2B_2)$ is ~ 16.7 K, similar to that previously reported.[1] The qualitative difference between the $\rho(T)$'s shown for the two (Fig. 3) is rather evident, regardless of the 10 to 20% impurity phases present in $(LuC)(Ni_2B_2)$. The ρ is generally smaller for the crystalline sample of $(LuC)_2(Ni_2B_2)$ than for $(LuC)(Ni_2B_2)$, e.g., at room temperature 36 $\mu\Omega$ cm for the former and 121 for the latter, respectively. There exists a distinct linear T term in $\rho(T)$ above ~ 120 K and a quadratic T^2 term below for $(LuC)_2(Ni_2B_2)$. On the other hand, the $\rho(T)$ of $(LuC)(Ni_2B_2)$ exhibits a large negative curvature and a large temperature dependence above ~ 25 K.

The dc magnetic susceptibility χ as a function of temperature measured at 5 G is shown in Fig. 4 for the two samples. Relative sharp superconducting transitions are clearly evident at ~ 2.9 and 16.5 K for $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$, respectively. The latter is similar to that previously observed.[2] The samples cooled in zero field show a magnetic shielding equal to $\sim 70-100\%$ of that of a perfect superconductor. They display a Meissner effect of $\sim 10\%$ of that of a perfect superconductor, on cooling in a field, perhaps due to flux trapping. All magnetizations are deduced based on the theoretical densities without the demagnetization corrections. The observation suggests that the superconducting is a bulk effect.

Under pressure, both ρ and the superconducting transition are rapidly shifted linearly downward for $(LuC)_2(Ni_2B_2)$ as shown in Fig. 5 but only slightly so for $(LuC)(Ni_2B_2)$. The pressure effects on ρ and T_c are summarized in Figs. 6 and 7, for the two compounds. The value of $d\ln\rho/dP$ at room temperature for $(LuC)_2(Ni_2B_2)$ is -9×10^{-2} GPa^{-1}, about 20 times that of $(LuC)(Ni_2B_2)$. The pressure effects dT_c/dP's are -0.14 K/GPa and -0.05 K/GPa for $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$, respectively.

By assuming that the impurity phases do not contribute significantly to the conductivity of $(LuC)(Ni_2B_2)$, the large negative curvature and the relatively large temperature dependence of $\rho(T)$ shown in Fig. 3 can be attributed to the close proximity of the Fermi surface to the density of states peak, similar to the $A15$ (Ref. 7) compounds. The high T_c of 17 K in this compound may therefore be understood. On the other hand, the absence of the large negative curvature, and the weaker temperature dependence in ρ of $(LuC)_2(Ni_2B_2)$ may suggest a lower density of states near the Fermi surface in this compound, resulting in its lower T_c of 2.9 K. The superconductivity in $(LuC)(Ni_2B_2)$ can be attributed greatly to the high density of states associated with the itinerant $3d$ electrons in the Ni atoms. The present observation implies that there must exist subtle difference between the Ni local environments in the two compounds (e.g., the hybridization between the Ni-$3d$ and the C-$2p$ electrons).

Under pressure, T_c decreases rapidly for $(LuC)_2(Ni_2B_2)$ as shown in Fig. 7. The relative pressure effect on the transition temperature ($d\ln T_c/dP$), which is a better measure of the pressure influence on the superconducting properties of a solid, is -4.7×10^{-2} GPa^{-1}. We ascribe such a large T_c suppression mainly to a possible band broadening, which leads to a decrease in the density of states at the Fermi surface. This appears to be consistent with the large suppression of ρ by pressure as shown in Fig. 6. The small pressure effect on the T_c of $(LuC)(Ni_2B_2)$, i.e., $d\ln T_c/dP = -0.3\times10^{-3}$ GPa^{-1} may be due to the insensitivity of its electronic structure of the compound to pressure, consistent with the small pressure effect on its ρ. The large difference in $d\ln T_c/dP$'s observed are also rather unexpected, based on their similar chemical bonding.[3] Since the Ni_2B_2 layers are rigid, the different pressure effects on T_c may result from the different inter-Ni_2B_2 layer compressibilities of the two compounds, i.e., greater for $(LuC)_2(Ni_2B_2)$ than for $(LuC)(Ni_2B_2)$.

In conclusion, we have studied $(LuC)_2(Ni_2B_2)$ and $(LuC)(Ni_2B_2)$ at ambient and high pressures. $(LuC)_2(Ni_2B_2)$ was found to be superconducting at an unexpectedly low $T_c \sim 2.9$ K. Under pressures, both ρ and T_c decreases rapidly for $(LuC)_2(Ni_2B_2)$ but only slightly for $(LuC)(Ni_2B_2)$. The observations can be explained in terms of a smaller but a more pressure-sensitive density of states at the Fermi surface of $(LuC)_2(Ni_2B_2)$. The decrease of this small density of states of $(LuC)_2(Ni_2B_2)$ under pressure may be associated with the pressure induced hybridization between the Ni-$3d$ and C-$2p$ electrons. The results suggest the possible existence of subtle differences between the local Ni environments in the two compounds.

Note: Upon completion of this work, we have learned of the work of L. F. Mattheis in which the band properties of both $(LuC)(Ni_2B_2)$ and $(LuC)_2(Ni_2B_2)$ were calculated. His results show that, while the Fermi level coincides with a density-of-states peak associated with the Ni($3d$) bands for $(LuC)(Ni_2B_2)$, there is no peak in the density of states near the Fermi level for $(LuC)_2(Ni_2B_2)$. This is consistent with our observations of a lower resistivity and a much lower T_c in $(LuC)_2(Ni_2B_2)$.

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