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The antipressure effect of Cu on T_c in superconducting $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ ($0 \leq x \leq 0.25$)

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Abstract

As observed with x-ray powder diffraction, the orthorhombic structure of the parent compound LaNiC_2 is retained in $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ up to the solubility limit near $x = 0.2$. The refined lattice parameters show that both the c -axis and the volume of the unit cell v expand clearly, while the a - and b -axes show less percentage change due to doping with copper. These results are inconsistent with what one would expect from a chemical pressure effect. The change in T_c with x is similar to the change in the lattice parameters (c and v) with x and is consistent with the assumption that Cu has finite solubility in this system. Magnetic measurements indicate that the increase in T_c is initially rapid ($dT_c/dx = 12$ K) but slows down ($dT_c/dx = 1$ K) for $x \geq 0.2$ in the system $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$. As expected from the BCS theory, the Cu doping in this system may affect not only the density of state $N(E_F)$, but also the electron–phonon coupling parameter.

1. Introduction

Superconductivity in nickel-based ternary or quaternary intermetallic compounds has been the focus of numerous recent experimental studies [1–14]. LaNiC_2 , which crystallizes in the orthorhombic CeNiC_2 -type structure with space group $Amm2$ [15], was found to be the first nickel-based ternary carbide superconductor with superconducting transition temperature $T_c \sim 2.7$ K [6, 16], as characterized by the specific heat, electrical resistivity and dc magnetic susceptibility data. Previous reports showed that about 50% substitution of La in LaNiC_2 with the 5f element thorium (Th) could enhance the T_c up to 7.9 K [7, 8]. Within a simple theoretical rigid-band model, the substitution of Th for La would be expected to shift the Fermi energy E_F to a higher level and hence also the density of state $N(E_F)$, since Th possesses one more free electron compared to La. However, earlier band-structure calculations for both $\text{LuNi}_2\text{B}_2\text{C}$ [17, 18] and $\text{YNi}_2\text{B}_2\text{C}$ [18] indicated that the major contribution to $N(E_F)$ came from the Ni 3d band and the Fermi level E_F near a peak in the density of states (DOE). This large value of $N(E_F)$,

together with a moderately strong electron–phonon coupling, were believed [17, 18] to be primarily responsible for the fairly high T_c s in the class of materials $\text{RNi}_2\text{B}_2\text{C}$ ($R = \text{rare earth}$). So far the highest superconducting transition temperature T_c observed in the Ni series is 16.6 K for $\text{LuNi}_2\text{B}_2\text{C}$ [2]. In this study, we explore the effects of Cu substitutions at the Ni site in the LaNiC_2 system. Since the Cu^+ (Cu^{2+}) ion has a larger (smaller) size than the Ni^{2+} ion, this pseudo-ternary system $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ provides an excellent opportunity to investigate the effects of alloying as well as antipressure (pressure) on the superconducting behavior in LaNiC_2 . It is noted here that the isostructural compound YNiC_2 , which may be treated as a pure chemical pressure effect of LaNiC_2 because of the smaller size of Y^{3+} than La^{3+} , exhibits no superconducting signal above 0.5 K in the low-temperature specific heat data [14].

2. Experimental details

Polycrystalline samples were prepared by conventional argon arc melting of stoichiometric amounts of the components on a water-cooled copper hearth. The 3N purity La, 4N purity Ni,

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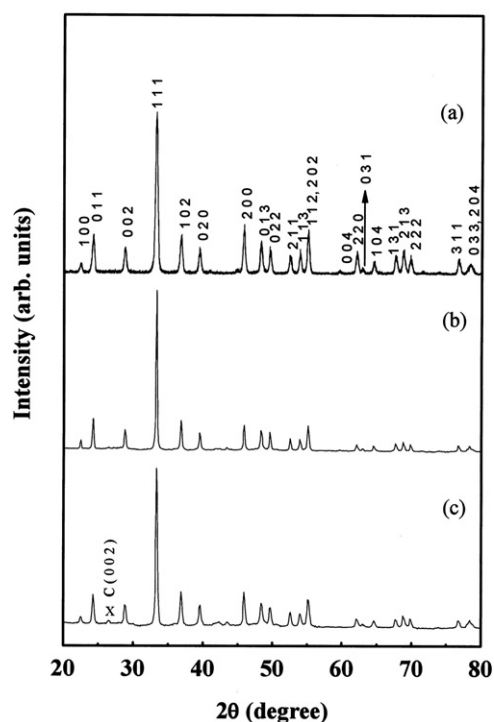


Figure 1. Room-temperature powder x-ray diffraction patterns of (a) LaNiC_2 , (b) $\text{La}(\text{Ni}_{0.8}\text{Cu}_{0.2})\text{C}_2$ and (c) $\text{La}(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{C}_2$ using $\text{Cu K}\alpha$ radiation.

6N purity Cu and 5N purity graphite (C) were purchased from CERAC. The resulting buttons were turned over and remelted five or six times to ensure good sample homogeneity. Due to the sufficiently low vapor pressures of these elements at melting temperature of the pseudo-ternary compounds, weight losses during arc melting were negligible ($<0.5\%$).

A microcomputer controlled MXP3 diffractometer equipped with copper target and graphite monochromator for $\text{Cu K}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) radiation was used to get the powder x-ray diffraction patterns. The crystallographic parameters were determined by using the PowderCell program [19]. Magnetic data were obtained using a commercial Quantum Design SQUID (Superconducting Quantum Interference Device) magnetometer. The temperature dependence of magnetization was obtained using a zero field cooling process, i.e. the sample was initially cooled in zero field (actually $\sim 5 \times 10^{-3} \text{ Oe}$) to 1.8 K and subsequently a small field ($\sim 10 \text{ Oe}$) was applied, and the zero field-cooled (ZFC) curve was taken as a function of increasing temperature up to $T > T_c$. A standard four-probe technique for dc electrical resistivity measurements was used with rectangular samples of uniform cross-sectional area (approximate size $1 \times 1 \times 6 \text{ mm}^3$) between 1.8 and 300 K in a system fully automated for temperature stability and data acquisition². A Keithley model 220 programmable current source was used as the constant current source and a Keithley model 182 nanovoltmeter was used to measure the output voltage. Data were taken with the current (10 mA) applied in both directions to eliminate possible thermoelectric

² Quantum Design, Inc, San Diego, CA 92121, USA.

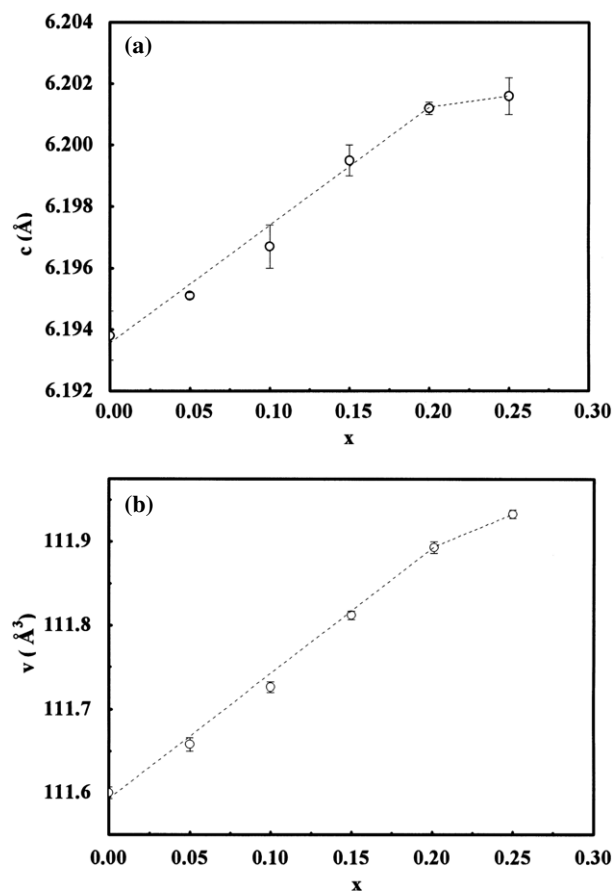


Figure 2. Variation of lattice parameters versus dopant concentration: (a) c versus x and (b) v versus x .

effects. Once the sample resistance R was measured, the resistivity ρ could be calculated using Ohm's law. The midpoint of the transition and 10–90% values were taken as the superconducting transition temperature T_c and transition width for both magnetic and electrical measurements. All data reported are from as-prepared samples.

3. Results and discussions

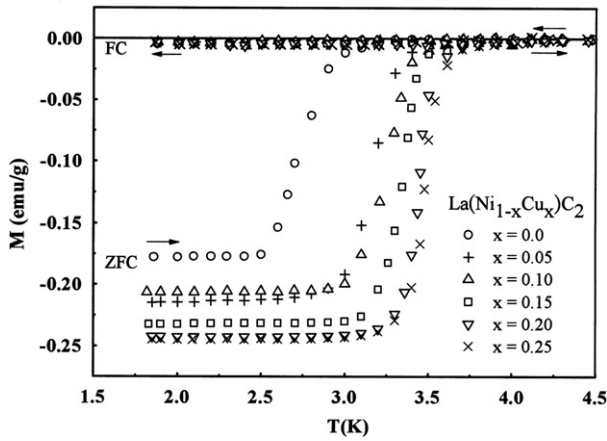
The observed powder x-ray diffraction patterns at room temperature for three representative samples LaNiC_2 , $\text{La}(\text{Ni}_{0.8}\text{Cu}_{0.2})\text{C}_2$, and $\text{La}(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{C}_2$ are shown in figures 1(a)–(c). It is found that the peaks of each observed pattern can all be indexed in an orthorhombic structure with space group $Amm2$ for the five samples in the series $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ with $x = 0, 0.05, 0.1, 0.15$ and 0.2 . The weak lines marked by \times in figure 1(c) for the sample with $x = 0.25$ is due to the impurity phase of C which has no effect on superconductivity. This demonstrates that the structure of the parent compound LaNiC_2 is retained in $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ up to the solubility limit $x \approx 0.2$. In fact, the phenomenon of a solubility limit is also reflected in the lattice parameter data. As presented in figures 2(a) and (b), a marked deviation from Vegard's law for the changes in the c and v parameters of the solid solution $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ occurs around $x = 0.20$, which seems to be an indication of an inhomogeneous Cu distribution

Table 1. Lattice parameters, T_c (10–90% values) and resistivity at $T = 300$ K in the series $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$. The number given in parentheses is the standard deviation in the least significant digit of the reported value.

Composition (x)	a (Å)	b (Å)	c (Å)	v (Å ³)	T_c^a (K)	T_c^b (K)	ρ (300 K) ($\mu\Omega$ cm)
0.0	3.954(1)	4.557(1)	6.193(8)	111.60(7)	2.63–2.86	3.07–3.45	191
0.05	3.954(4)	4.557(9)	6.195(1)	111.65(9)	2.98–3.15	3.15–4.05	168
0.10	3.954(9)	4.558(9)	6.196(7)	111.72(6)	3.08–3.24	3.45–4.21	120
0.15	3.955(9)	4.559(1)	6.199(5)	111.81(2)	3.19–3.31	3.72–4.25	107
0.20	3.956(9)	4.560(1)	6.201(2)	111.89(3)	3.32–3.45	4.02–4.61	90
0.25	3.957(7)	4.560(5)	6.201(6)	111.93(3)	3.37–3.48	4.05–4.65	107

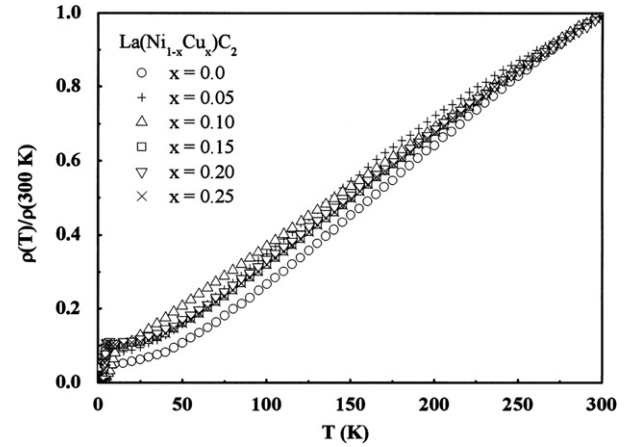
^a Determined by dc magnetization measurement, $H_{dc} = 10$ Oe.

^b Determined by dc electrical measurement.

**Figure 3.** Temperature dependence of ZFC and FC magnetization data for six compounds in the series $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ ($x = 0, 0.05, 0.1, 0.15, 0.2$ and 0.25) measured in a field of 10 Oe between 1.8 and 4.5 K.

at higher concentrations due to an approaching solubility limit. The refined lattice parameters a , b , c and v of the unit cell, determined by the method of least squares using the 20 intense reflections for $2\theta < 80^\circ$, are listed in table 1. Unlike the crystallographic parameters c and v , the a and b lattice parameters show a smaller percentage change.

Figure 3 displays the temperature dependence of the ZFC and field-cooled (FC) magnetization for the six samples in the series $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ ($0 \leq x \leq 0.25$) measured in a field of 10 Oe between 1.8 and 4.5 K. All measurements were performed on bulk samples with a mass of about 0.3 g. It is seen that the shielding curves for constant field shift toward a higher temperature region with increasing Cu concentration up to $x = 0.25$. The increase in T_c is initially fast ($dT_c/dx = 12$ K) but slows down for the sample with $x > 0.2$ ($dT_c/dx = 1$ K). No data appear here for the sample with $x > 0.25$ because of its worse powder x-ray diffraction (more impurity phase) and worse superconducting signal. Since all the ZFC curves show a sharp transition and reach saturation at the lower temperature, the superconducting phase homogeneity looks good in these samples. As observed in figure 3, each magnetization curve also shows large shielding signals, in comparison to the ideal value of $-1/4\pi$ for a long cylinder, with apparent volume fractions above 100%. We can explain

**Figure 4.** Resistivity normalized at 300 K versus T for six alloys in the system $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$. Six symbols (\circ , $+$, \triangle , \square , ∇ , \times) correspond to the samples $x = 0, 0.05, 0.1, 0.15, 0.2$ and 0.25 , respectively.

this phenomenon in terms of the shielding current and the geometrical demagnetization factor because of the irregular-shaped samples. The lower Meissner flux expulsion from FC data for all samples in figure 3 is characteristic of a pinning effect in the superconducting material.

The complete normalized resistivity data between 1.8 and 300 K for six alloys in the series $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ are presented in figure 4. All compounds display similarly shaped ρ versus T curves. The room-temperature resistivity versus composition dependence as listed in table 1 reflects no regular tendency, probably due to the substitution effect of disordered positions of the Ni and Cu atoms. The residual resistivity ratio ($\rho_{300}/\rho_{5.0} = \Gamma_{5.0}$) for the samples is between 9.4 (for the sample with $x = 2.0$) and 21 (for the parent compound), which indicates that the crystallinity and purity of the samples investigated are not bad because values above 10 are considered to be a good indicator of the crystallinity and purity of a stoichiometric intermetallic compound. The zero resistance temperature shown in figure 5 are 3.0, 3.2, 3.4, 3.6, 3.9 and 3.9 K for the samples with $x = 0, 0.05, 0.10, 0.15, 0.20$ and 0.25 , respectively. It is noticed that the zero resistance temperatures for the compounds are slightly higher than the transition point value obtained by magnetic measurements. The phenomenon is probably due to the surface

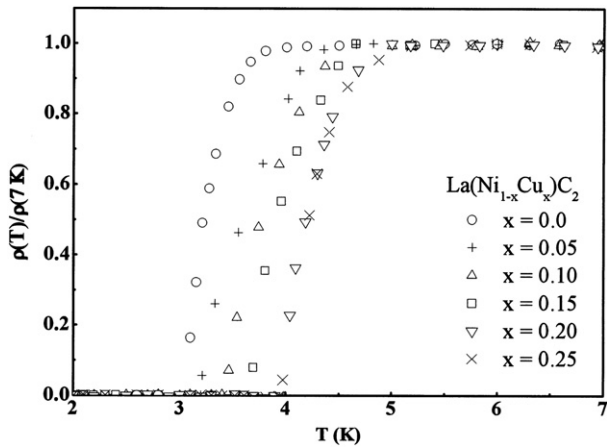


Figure 5. Resistivity normalized at 7 K versus T for six alloys in the system $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$. Six symbols (\circ , $+$, \triangle , \square , ∇ , \times) correspond to the samples $x = 0, 0.05, 0.1, 0.15, 0.2$ and 0.25 , respectively.

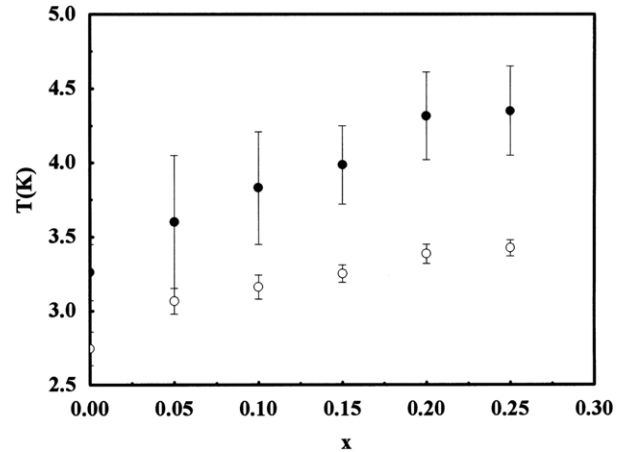


Figure 6. Superconducting transition temperature T_c (10–90% value) as a function of Cu constituent in the system $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$. Two symbols (\circ , \bullet) correspond to magnetic and electrical data, respectively.

superconductivity [20, 21] of these compounds, or due to the different effective time scales involved in magnetic and electric measurements. The critical temperature T_c (10–90% value) as determined by two types of experiments (χ_{dc} and ρ) are plotted as a function of Cu content x in figure 6. An interesting observation is that the T_c value increases rapidly first with Cu content x up to 0.2 then goes flat, which appears to be an outward manifestation of the solubility limit in $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$.

Because the lattice parameters c and v increase smoothly up to $x = 0.2$ as a result of substitution of Ni with Cu and the $\text{Cu}^{1+}(\text{Cu}^{2+})$ ion has a larger (smaller) size than the Ni^{2+} ion, it is supposed that the Cu ion valence in the pseudo-ternary system $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ is $+1$ from the viewpoint of lattice expansion. Comparing the crystallographic parameters and T_c values, one aspect of substitution with Cu in this system needs some consideration. As can be seen in figures 2(a) and (b), the expansion of the c -axis and unit cell volume v with x is initially rapid, but slows down for $x \geq 0.2$. For the sample with $x = 0.25$, the relative intensities of impurity peaks in XRD also appear. These observations indicate that the solubility limit of copper in this compound lies near $x = 0.2$. This conjecture is further supported by the dependence of the increase in T_c on x , as shown in figure 6. According to the simple BCS (Bardeen, Cooper, Schrieffer) prediction, in zero magnetic field superconducting ordering sets in at a critical temperature given by [22]

$$k_B T_c = 1.13 \hbar \omega_{\text{ph}} \exp(-1/N_0 V_0)$$

where N_0 is the density of electronic levels for a single spin population in the normal metal. For weak coupling V_0 , $N_0 V_0 = N(E_F) V_0 = 1/2 g(E_F) V_0$ is observed in the range from 0.1 to 0.5. Remembering that the phonon frequency $\omega_{\text{ph}} \propto m_{\text{ion}}^{-1/2}$. If T_c is dominated by the phonon frequency, then T_c will decrease with the doping of Cu in the series of $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ because of the larger mass of the Cu ion compared to Ni. Therefore the other factor $N(E_F) V_0$ in the above BCS formula should

have a more important effect on the increase in T_c in the system $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$. The softening of the lattice under antipressure and the decrease of charge density will change both the electron–phonon coupling strength V_0 and the electron density of state at the Fermi level, $N(E_F)$, leading to the change of T_c value.

4. Conclusions

In conclusion, we report the results of our investigations in $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)\text{C}_2$ ($0 \leq x \leq 0.25$), a new pseudo-ternary series with CeNiC_2 -type orthorhombic structure. From the present study, we infer that the expansion of the volume of the unit cell or the chemical antipressure effect of Cu is favorable, with respect to pure LaNiC_2 , to the superconducting transition temperature T_c . This result is contrary to what is observed in the superconducting system $\text{Y}(\text{Ni}_{2-x}\text{Cu}_x)\text{B}_2\text{C}$ [5] in which T_c drops with x irrespective of the expansion of the volume of the unit cell, probably due to a shift of $N(E_F)$ from the maximum density of state in the parent compound $\text{YNi}_2\text{B}_2\text{C}$.

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