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Effect of Ni-site substitutions in superconducting $La_3Ni_2B_2N_{3-\delta}$

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We investigated the effect of Ni/Co and Ni/Cu substitutions upon the superconducting and normal state properties of $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$ ($M=$ Co, Cu). X-ray and neutron diffraction studies reveal a limited solid solubility for Cu: ($0<x_{\mathrm{Cu}}\leqslant 0.1$) and single phase compounds for $0<x_{\mathrm{Co}}\leqslant 0.3$. From ac-, dc-susceptibility, and specific heat measurements we determined T_c, the bare density of states at the Fermi energy $N(E_f)$, the electron-phonon mass enhancement λ, and the Stoner enhancement factor S, as a function of x. Superconductivity is suppressed to below 1.5 K for $La_3(Ni_{0.7}Co_{0.3})_2B_2N_{3-\delta}$ while for Ni/Cu substitution only the initial depression rate, $dT_c/dx\simeq -0.23$ K/(mol % Cu), could be determined. The results clearly show that the suppression of superconductivity is primarily caused by the reduction of $N(E_f)$ concomitant with a fall of the coupling strength λ, while there are no hints for other effects like magnetic pair breaking. The comparison with the results reported for $Y(Ni_{1-x}Co_x)_2B_2C$ shows that the electronic changes induced by Ni/Co substitution are very similar in both systems. [S0163-1829(98)04045-4]

I. INTRODUCTION

$La_3Ni_2B_2N_{3-\delta}$ is superconducting (SC) below 12 K and crystallizes in the body-centered tetragonal structure consisting of Ni_2B_2 layers built from NiB_4 tetrahedra separated by three LaN rocksalt-type layers and belongs to the family of new lanthanum nickel boronitrides $(LaN)_nNi_2B_2$ with $n=2,3$.[1,2] Both quaternary boronitride compounds are isostructural with the homologous borocarbide series $(YC)_nNi_2B_2$ ($n=1,\ldots,4$).[3] Their structure is body-centered (for n odd) or simple tetragonal (for n even) with n LaN or YC rocksalt-type layers. While the two layer compound LaNiBN is a normal conducting metal down to 4.2 K, we characterized $La_3Ni_2B_2N_{3-\delta}$ ($T_c\simeq 12$ K) as a weak-coupling BCS superconductor.[4]

For the borocarbide superconductors Ni/Co substitution, e.g., in $Y(Ni_{1-x}Co_x)_2B_2C$, yields a drastic decrease of T_c,[5–8] while in the case of the nonsuperconducting YNiBC compound superconductivity could be recovered by proper Ni/Cu substitution ($T_c\simeq 8$ K for $YNi_{0.4}Cu_{0.6}BC$).[9] The aim of this paper addresses the question of whether T_c could be raised by proper metal substitutions in the triple layer boronitrides.

II. EXPERIMENTAL

Polycrystalline samples were arc melted from lanthanum ingots (Auer-Remy, D, 99.9%), Co, Ni, and Cu powder or ingots (Alfa-Ventron, D, 99.9%), hexagonal boron nitride powder (Johnson Matthey & Co., GB, 99.8%) and ^{11}BN powder (98% enriched ^{11}B, chemical purity >98%, Centronic Ltd., Crydon, GB). Details of the melting and annealing procedure were given in a previous report.[4] A large specimen of $La_3(Ni_{0.7}Co_{0.3})_2{}^{11}B_2N_{3-\delta}$ ($\simeq 5$ g) with isotope enriched ^{11}BN powder was prepared for neutron investigations. A small quantity of each sample was powdered under cyclohexane, sealed in thin quartz capillaries and exposed to Cr-K_α radiation ($\lambda_{K_{\alpha 1}}=0.228970$ nm) in a Debye-Scherrer camera. Precise lattice parameters were determined by means of a least squares refinement of Guinier-Huber photographs with Cu-$K_{\alpha 1}$ radiation ($\lambda=0.1540562$ nm) using an internal Ge standard, $a_{\mathrm{Ge}}=0.5657906$ nm.

Neutron powder diffraction at 300 K was performed at the ORPHEE 14 MW reactor (CEA-Saclay) using the 3T2 double-axis multidetector neutron powder diffractometer (wavelength $\lambda_n=0.1227$ nm, resolution $\Delta d/d\geqslant 4\times 10^{-3}$, see Ref. 10). Preferred orientation effects were minimized by powdering the sample in a steel mortar to a grain size smaller than 30 μm. Further details concerning the experiment are given in Sec. III A (see Table II). Precise atom parameters, occupation numbers, individual isotropic thermal factors, and profile parameters were derived from a least squares full matrix Rietveld refinement routine.[11,12] Neutron scattering lengths were taken from a recent compilation by Sears.[13]

Ac- and dc-susceptibility measurements were performed in a calibrated ac susceptometer (80 Hz and field amplitudes up to 1 mT) and in a 6 T superconducting quantum interference device magnetometer, respectively. Specific heat measurements in the temperature range 1.5–80 K and with magnetic fields up to 9 T were carried out on 2–3 g samples employing a quasiadiabatic step heating technique.

III. RESULTS

A. Crystallographic characterization

X-ray photographs of $La_3(Ni_{1-x}Co_x)_2B_2N_{3-\delta}$ with $x=0-0.3$ and $La_3(Ni_{0.9}Cu_{0.1})_2B_2N_{3-\delta}$ revealed an intensity

TABLE I. The lattice parameters of $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$ obtained from the Guinier-Huber photographs.

M_x	a (nm)	c (nm)	V (nm^3)	c/a
	0.3721(3)	2.0520(5)	0.2842(1)	5.51
$Co_{0.1}$	0.37226(3)	2.049(1)	0.2840(2)	5.51
$Co_{0.2}$	0.37232(3)	2.045(1)	0.2835(1)	5.49
$Co_{0.3}$	0.372551(4)	2.042(1)	0.2834(1)	5.48
$Cu_{0.1}$	0.37205(4)	2.0553(7)	0.2845(1)	5.52

pattern which was successfully and completely indexed on the basis of the crystal structure of $La_3Ni_2B_2N_3$ (see Ref. 14) in combination with small amounts of secondary phases (mainly unreacted BN). Samples with the nominal composition $La_3(Ni_{1-x}Cu_x)_2B_2N_{3-\delta}$ with a larger Cu content ($x = 0.2$, 0.3) were found to be multiphase indicating that the solubility of copper is significantly lower than that of cobalt for which even a $La_3Co_2B_2N_3$ phase was reported.[15] Attempts to prepare samples with a nominal composition $LaTBN_{1+x}$ and $La_3T_2B_2N_{2+x}$ where Ni should be replaced by the $4d$ or $5d$ metal Pd or Pt yielded multiphase samples whose x-ray patterns could not be indexed. We note the absence of superconductivity down to 4.2 K even in traces.

The lattice parameters obtained for the single phase specimens of the series $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$ with $M = Co$ and Cu are collected in Table I. The remarkable trends outlined in Fig. 1 are the counteracting variation of the a and c lattice parameters ($d \ln a/dx \simeq +3.4 \times 10^{-3}$ and $d \ln c/dx \simeq -16 \times 10^{-3}$ taking x to be negative for Cu) which was also observed in the $Lu(Ni_{1-x}Co_x)_2B_2C$ system[16] and as an effect of rare-earth substitution in the borocarbides.[17] There is a slight increase of the volume when Cu replaces the Ni atoms, but V decreases upon Co substitution ($d \ln V/dx \simeq -10 \times 10^{-3}$). Both effects, the anomalous variation of the lattice parameters and the corresponding volume change can not be explained by the simple argument of chemical pressure. It seems that in the case of Ni/transition-metal substitution in $La_3Ni_2B_2N_{3-\delta}$ the atomic volumes of the $3d$ elements discard their usually observed anomaly for Mn, Fe, Co and seem to correlate well with the $4d$, $5d$ series revealing for the ‘‘normal’’ $3d$ series a pronounced minimum at six d electrons ($V_{Fe} < V_{Co} < V_{Ni} < V_{Cu} < V_{Zn}$); see Ref. 18.

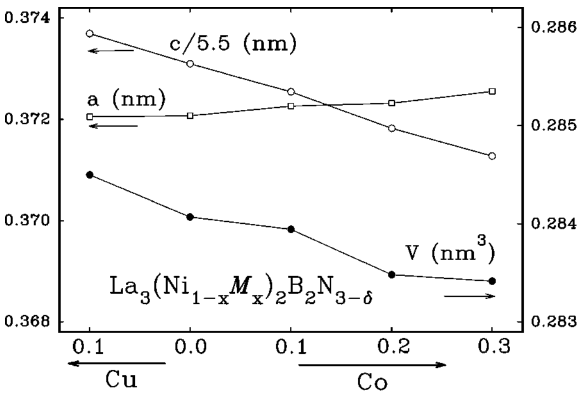

FIG. 1. The variation of the lattice parameters and the volume of $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$ with $M = Co$ to the right and $M = Cu$ on the left hand side.

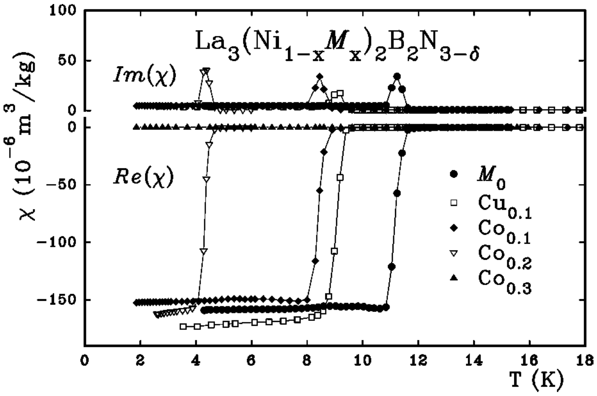

FIG. 2. Real and imaginary part of the ac susceptibility χ of $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$ measured with an 80 Hz ac-field amplitude of 200 A/m.

The result of the structure refinement of the neutron powder diffraction data of $La_3(Ni_{0.7}Co_{0.3})_2{}^{11}B_2N_{3-\delta}$ is listed in Table II and compares well with the data for the $La_3Ni_2B_2N_{3-\delta}$ parent compound (neutron data by Huang *et al.*[14]). The interatomic distances reflect the typical bonding characteristics of the $La_3Ni_2B_2N_{3-\delta}$ structure type, for which the tetragonal double pyramids $[La_5B]N$, the octahedra $[La_6]N$ and the archimedian antiprisms $[La_4Ni(Co)_4]B$ were identified as the essential structural chemical units formed around the nonmetal atoms (see Ref. 4). The refinement of the nitrogen positions in $La_3Ni_2{}^{11}B_2N_{3-\delta}$ by Huang *et al.*[14] as in $La_3(Ni_{0.7}Co_{0.3})_2{}^{11}B_2N_{3-\delta}$ yields a full occupation of the $4e$ site but a ~10% vacancy of the $2b$ site located in the central layer of the $(LaN)_3$ rock-salt type block. Thus, $\delta \approx 0.1$ remains rather constant within the $La_3(Ni, Co)_2B_2N_{3-\delta}$ series. The inverse variation of the a and c lattice parameter, i.e., the accommodation of the B-Ni-B bond angle seems to correlate with the number of d electrons on the Ni site.

B. Susceptibility and specific-heat measurements

The SC transition temperatures as well as the Meissner fractions were checked by ac-susceptibility measurements (see Fig. 2) on roughly bar shaped samples. The reproducibility of the T_c values of separately prepared $La_3Ni_2B_2N_{3-\delta}$ specimens is $(11.7) \pm 0.5$ K. As bandstructure calculations by Mattheiss[20] showed that the electronic density of states at the Fermi energy $N(E_f)$ is rather sensitive to a N-deficiency δ, we suppose that variations of the overall nitrogen stoichiometry may effect T_c by about ± 0.5 K. For clarity, we show only the data of one $La_3Ni_2B_2N_{3-\delta}$ sample (see also Ref. 4), because the small variation of T_c does not effect the discussion below.

$La_3(Ni_{0.7}Co_{0.3})_2B_2N_{3-\delta}$ is not superconducting down to 1.8 K while all other samples show bulk superconductivity with a diamagnetic signal which is in agreement with the value expected for perfect shielding (taking into account the demagnetization due to the macroscopic sample geometry, $D \sim 0.15-0.25$). Hence, Co substitution causes a systematic suppression of superconductivity in $La_3Ni_2B_2N_{3-\delta}$, without a significant broadening of the transition. The approximate slope of T_c versus the Co concentration is $dT_c/dx \simeq -0.3$ K/(mol %Co). A reduction of T_c is also seen for $La_3(Ni_{0.9}Cu_{0.1})_2B_2N_{3-\delta}$.

TABLE II. Neutron structure refinement data of $La_3(Ni_{0.7}Co_{0.3})_2B_2N_{3-\delta}$ and $La_3Ni_2B_2N_{3-\delta}$; details of the experiment and the various reliability factors are included. I_i is the integrated intensity of reflection i, Y_i is the number of counts (background corrected) at 2Θ, w_i is the weighting function; c is the scale factor, N is the number of points in the pattern, P are the refined parameters, and C are the constraint functions.

$La_3Ni_2B_2N_3$—Type, $Z=2$; Space Group $I4/mmm$—D_{4h}^{17}, origin at center;
standardized settings calculated with program STRUCTURE TIDY (Ref. 19).

Parameter/Compound	$La_3Ni_2B_2N_3$ (data after Ref. 14)	$La_3(Ni_{0.7}Co_{0.3})_2B_2N_3$ (this work)
Neutron wavelength	$\lambda_n=0.1417$ nm	$\lambda_n=0.1227$ nm
Absorption correction	$\mu R=0.13$	$\mu R=0.08$
2Θ-Range [deg.]	11–135, steps 0.05°	18.5–125.7, steps 0.05°
Number of reflections in refinement		176
Number of variables in refinement		23
Residual values:		
$R_e=[(N-P+C)/\Sigma\omega_i Y_i^{\mathrm{obs}2}]^{1/2}$		0.052
$\chi^2=(R_{wP}/R_e)^2$	1.90	4.84
$R_P=\sum\left\lvert Y_i^{\mathrm{obs}}-\frac{1}{c}Y_i^{\mathrm{calc}}\right\rvert\Big/\sum Y_i^{\mathrm{obs}}$	0.057	0.082
$R_F=\sum\left\lvert I_i^{\mathrm{obs}1/2}-\frac{1}{c}I_i^{\mathrm{calc}1/2}\right\rvert\Big/\sum I_i^{\mathrm{obs}1/2}$		0.056
$R_I=\sum\left\lvert I_i^{\mathrm{obs}}-\frac{1}{c}I_i^{\mathrm{calc}}\right\rvert\Big/\sum \lvert I_i^{\mathrm{obs}}\rvert$		0.065
Preferred orientation		−0.05(1), [110]
Lattice parameters [nm]	$a=0.37251(1)$	$a=0.37230(1)$
	$c=2.05172(4)$	$c=2.04289(8)$
Atom parameters		
La1 in $4e$ $(0,0,z)$	$z=0.3705(1)$	$z=0.3698(1)$
$B_{\mathrm{eq}}(B_{\mathrm{iso}})10^2$ in nm^2	0.43(5)	0.20(4)
La2 in $2a$ (0,0,0)	$B_{\mathrm{eq}}=0.60(7)$	0.20(4)
$(Ni_{0.7}Co_{0.3})$ in $4d$ (0,0.5,0.25)	0.64(3)	0.41(5)
N1 in $4e$ $(0,0,z)$	$z=0.1246(1)$	$z=0.1244(1)$
$B_{\mathrm{eq}}(B_{\mathrm{iso}})10^2$ in nm^2	0.58(5)	0.64(5)
N2 in $2b$ (0,0,0.5)	occ.=0.92(1)	occ.=0.89(1)
$B_{\mathrm{eq}}(B_{\mathrm{iso}})10^2$ in nm^2	0.5(1)	0.64(5)
B in $4e$ $(0,0,z)$	$z=0.1946(2)$	$z=0.1964(2)$
$B_{\mathrm{eq}}(B_{\mathrm{iso}})10^2$ in nm^2	0.76(4)	0.62(6)

Interatomic distances in nm (±0.0006 nm)		$La_3Ni_2B_2N_3$ data after Ref. 14	$La_3(Ni_{0.7}Co_{0.3})_2B_2N_3$ this work
La1	−4La1	0.3719	0.3723
	−4La2	0.3738	0.3743
	−4Ni	0.3093	0.3075
	−4B	0.2949	0.2959
	−4N1	0.2632	0.2635
	−1N2	0.2656	0.2660
La2	−8La1	0.3738	0.3723
	−4La2	0.3719	0.3743
	−2N1	0.2556	0.2542
	−4N2	0.2630	0.2633
Ni	−4La1	0.3093	0.3075
	−4Ni	0.2630	0.2633
	−4B	0.2179	0.2160
B	−4La1	0.2949	0.2959
	−4Ni	0.2179	0.2160
	−1N1	0.1436	0.1470
N1	−4La1	0.2632	0.2635
	−1La2	0.2556	0.2542
	−1B	0.1436	0.1470
N2	−2La1	0.2656	0.2660

TABLE II. (*Continued*).

Interatomic distances in nm (± 0.0006 nm)	$La_3Ni_2B_2N_3$ data after Ref. 14	$La_3(Ni_{0.7}Co_{0.3})_2B_2N_3$ this work
-4La2	0.2630	0.2633
Bonding angles, in degrees		
N-B-Ni	121.39	120.48
Ni-B-Ni	74.25	75.09
B-Ni-B	117.21	119.04
B-Ni-B	105.75	104.91
N-B-La	63.08	62.82

The normal state static susceptibility of the series $La_3(Ni_{1-x}Co_x)_2B_2N_{3-\delta}$ studied by dc-magnetization measurements is shown in Fig. 3. A reasonable description of the data is obtained by the combination of a Stoner-Wohlfarth susceptibility and a Curie-Weiss term $\chi(T)=\chi_0(1+aT^2)+C/(T-\Theta)$, yielding χ_0 values ranging from 4.1–5.4 $\times 10^{-7}$ emu/g. For all samples except that with $Cu_{0.1}$ we obtain similar Curie constants, $C\sim 6\times 10^{-6}$ emu K/g, and paramagnetic Curie temperatures of the order of -10 K. This paramagnetic contribution corresponding to an effective magnetic moment $\mu_{\mathrm{eff}}\simeq 0.16(2)\mu_{\mathrm{B}}$/f.u. is of the same magnitude as that found in Y(Ni, Co)$_2$B$_2$C (e.g., Ref. 8) and can be attributed to paramagnetic impurities rather than to be an intrinsic property of the boronitride and borocarbide phases. The susceptibility of $La_3(Ni_{0.9}Cu_{0.1})_2B_2N_{3-\delta}$ shows a significantly larger paramagnetic contribution corresponding to an effective moment, $\mu_{\mathrm{eff}}\simeq 0.3\mu_{\mathrm{B}}$/f.u., which indicates that the sample quality is not as good as that of the (Ni, Co) series. This could be related to the limited solubility of copper in this compound. Nevertheless, $\chi_0\simeq 4.15\times 10^{-7}$ emu/g is very close to the values obtained for $La_3Ni_2B_2N_{3-\delta}$ and $La_3(Ni_{0.9}Co_{0.1})_2B_2N_{3-\delta}$. The variation of χ_0 yields different trends as the electronic specific heat shown below and is discussed in Sec. IV.

The low-temperature specific heat results of the $La_3(Ni,\ M)_2B_2N_{3-\delta}$ series are depicted in Fig. 4 in a C_p/T vs T^2 representation. In accordance with the susceptibility data all samples [except non-SC $La_3(Ni_{0.7}Co_{0.3})_2B_2N_{3-\delta}$] show a second order transition from the SC to the normal state heat capacity, $C_p=C_e+C_{ph}\simeq\gamma T+\beta T^3$, where γ is the Sommerfeld parameter and β is related to the low-temperature value of the Debye temperature by $\Theta_D^{\mathrm{LT}}=(1944\times 10/\beta)^{1/3}$. For $La_3Ni_2B_2N_{3-\delta}$ and $La_3(Ni_{0.9}M_{0.1})_2B_2N_{3-\delta}$ ($M=$Co, Cu) high-field data (9 T, not shown) were used to analyze the normal state specific heat, because SC is fully suppressed by the applied field.[4] By a low-temperature linear fit of the normal state heat capacity $C_p/T(T^2)$ we determined the γ and Θ_D^{LT} values summarized in Table III which also includes the thermodynamic mean value of the transition temperatures T_c and the height of the specific heat jumps $\Delta C\equiv C_s(T_c)-C_n(T_c)$. The latter two values are obtained by idealizing the second order anomaly under the constraint of entropy balance between the SC and the normal state to an infinitely sharp transition.

The overall temperature dependence of the specific heat $C_p/T(T)$ is shown in Fig. 5. Within the series $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$ there is hardly a change of the temperature dependence of the lattice heat capacities above 10 K. Even at 80 K the absolute values of the heat capacities differ mainly due to the different electronic contributions. This indicates that the spectral moment of the phonon density of states $F(\omega)$ which is $\overline{\omega_2}\simeq 333$ K for $La_3Ni_2B_2N_{3-\delta}$ (see Ref. 4) remains rather unchanged. Hence, the effect of Ni-site substitution upon the phonon density of states $F(\omega)$ is less pronounced than indicated by the increase of the Debye temperature $\Theta_{\mathrm{D}}^{\mathrm{LT}}$ values derived from the low-temperature regime (see Table III). Note, the overall temperature dependence of the lattice heat capacities reflects the full phonon spectrum $F(\omega)$, whereas the low-temperature $\Theta_{\mathrm{D}}^{\mathrm{LT}}$ values are primarily a measure for the low-energy (acoustic, small q) phonon modes which may show a temperature dependence due to the electron-phonon interaction.[21] In a previous work,[4] we pointed out that the slope of the normal state heat capacity C_p/T vs T^2 of $La_3Ni_2B_2N_{3-\delta}$ changes significantly at about $T_c/2$ indicating that $\Theta_{\mathrm{D}}^{\mathrm{LT}}$ increases from 303 K (determined in the temperature interval 2–5 K) to about 345 K (at 7–12 K)—such a kind of behavior was also reported for Nb_3Sn.[22] The normal state heat capacity of $La_3(Ni_{0.9}M_{0.1})_2B_2N_{3-\delta}$ ($M=$Co, Cu) also indicates a small increase of $\Theta_{\mathrm{D}}^{\mathrm{LT}}$ by about 10 K, but this kind of feature does not show up in non-SC $La_3(Ni_{0.7}Co_{0.3})_2B_2N_{3-\delta}$ (see Fig. 4). Hence, we suggest that the pronounced increase of $\Theta_{\mathrm{D}}^{\mathrm{LT}}$ (from 303 to 372 K) is

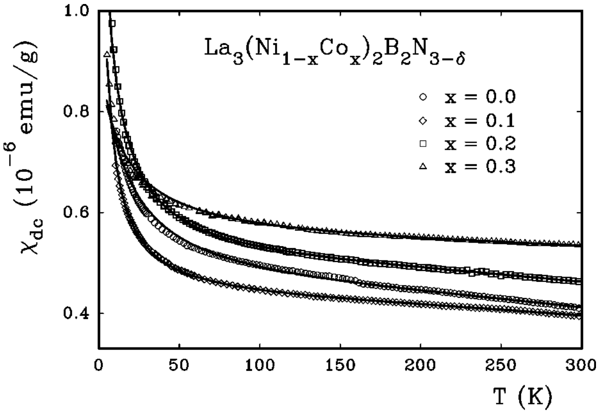

FIG. 3. The static susceptibility χ_{dc} of $La_3(Ni_{1-x}Co_x)_2B_2N_{3-\delta}$ measured at a field of 1 T; the solid lines are the resulting fits (see text).

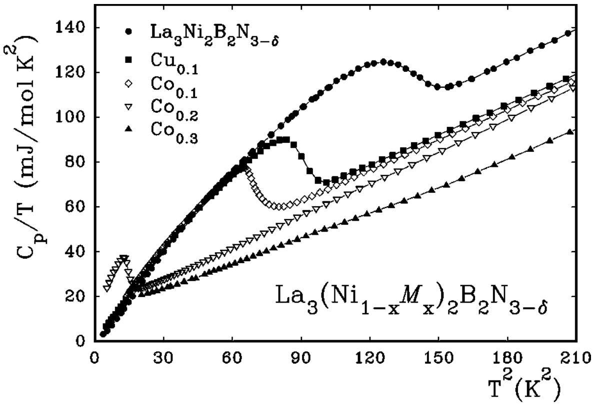

FIG. 4. The low-temperature specific heat C_p/T vs T^2 of $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$ (M=Co, Cu) measured in zero field.

partly related to a weakening of electron-phonon interactions and to a (minor) lattice stiffening (345 to 372 K) due to mass and/or volume reduction.

IV. DISCUSSION

In the specific heat results presented in Sec. III B Ni/Co(Cu) substitution yielded a clear reduction of the normal state electronic heat capacity $C_{\mathrm{el}}=\gamma T$ which is related to the electronic density of states at the Fermi level $N(E_f)$ by

$$C_{\mathrm{el}}(T)=\gamma T=\frac{\pi^2}{3}k_{\mathrm{B}}^2(1+\lambda)N(E_f)T, \tag{1}$$

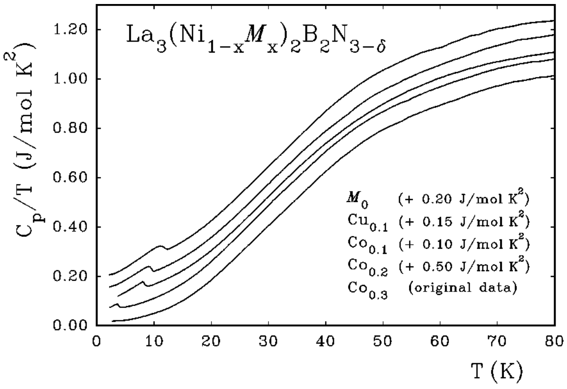

FIG. 5. The specific heat $C_p/T(T)$ of $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$ (M=Co, Cu). For clarity, the curves are sequentially shifted by 0.05 J/mol K^2 as labeled, i.e., the lowest curve corresponds to $La_3(Ni_{0.7}Co_{0.3})_2B_2N_{3-\delta}$ and the uppermost curve represents $La_3Ni_2B_2N_{3-\delta}$ having added 0.2 J/mol K^2.

where λ is the enhancement of the effective electron mass due to the electron-phonon interaction. In the case of $La_3Ni_2B_2N_{3-\delta}$ a comparison of the measured $\gamma=26$ mJ/mol K^2 with the γ_{bs} value according to the calculated bare density of states gives $\lambda\equiv\gamma/\gamma_{bs}-1=0.85$, a value which is also obtained with the McMillan formula[23]

$$T_c=\frac{\Theta_{\mathrm{D}}}{1.45}\exp\left(-\frac{1.04(1+\lambda)}{\lambda-\mu^\star(1+0.62\lambda)}\right), \tag{2}$$

where $T_c=11.7$ K, $\Theta_{\mathrm{D}}=303$ K, and $\mu^\star\simeq0.13$ yields again $\lambda\simeq0.85$ (see also Ref. 4). Hence, the significant reduction of the electronic specific heat due to Co doping is caused by a reduction of the density of states $N(E_f)$ and/or the decrease of the electron-phonon mass enhancement λ which is obvious from the decrease of T_c. In order to disentangle these two effects, we evaluated λ with relation 2 (using the common approximation for the Coulomb pseudopotential $\mu^\star\simeq0.13$) and accordingly obtained the bare density of states $N(E_f)$ from relation 1. Both, the electronic density of states $N(E_f)$ and the λ values summarized in Table IV account for the reduction of the γ value with increasing Co content. There is a further relation between the electronic density of states and the electron-phonon coupling strength parameter given by

$$\lambda=\frac{N(E_f)\langle I^2\rangle}{M\overline{\omega_2^2}} \tag{3}$$

with $\langle I^2\rangle$ the average of the electron-phonon matrix elements and M the mean atomic mass.[23] In the case of $La_3(Ni_{0.9}Cu_{0.1})_2B_2N_{3-\delta}$ the relative change of the $N(E_f)$ and λ value with respect to $La_3Ni_2B_2N_{3-\delta}$ is too small to check the applicability of relation (3). However, for the $La_3(Ni_{1-x}Co_x)_2B_2N_{3-\delta}$ series it is obvious that the electron-phonon mass enhancement λ scales clearly with the electronic density of states $N(E_f)$ while changes of the mean matrix element $\langle I^2\rangle$ and the characteristic frequency $\overline{\omega_2}$ are of minor importance. Hence, we conclude that the suppression of superconductivity in $La_3(Ni_{1-x}Co_x)_2B_2N_{3-\delta}$ is primarily related to the reduction of $N(E_f)$.

TABLE III. Characteristic values obtained from the superconducting and normal state specific heat data of $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$ (see text).

M_x	T_c (K)	γ (mJ/mol K^2)	Θ_{D}^{LT} (K)	ΔC (J/mol K)
	11.7	26(1)	303(3)	0.43(2)
$Co_{0.1}$	8.35	20.5(8)	352(3)	0.25(2)
$Co_{0.2}$	3.85	15(2)	362(4)	0.08(1)
$Co_{0.3}$	<1.5	14(2)	372(5)	
$Cu_{0.1}$	9.40	24.5(5)	347(3)	0.30(2)

TABLE IV. The estimated bare electronic density of states, $N(E_f)$ of $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$ (assuming the band mass to be close to 1), and the electron-phonon mass enhancement λ values.

	$N(E_f)$ (states/eV cell)	λ
$La_3Ni_2B_2N_{3-\delta}$	6.0(2)	0.85(5)
$La_3(Ni_{0.9}Co_{0.1})_2B_2N_{3-\delta}$	5.1(2)	0.71(5)
$La_3(Ni_{0.8}Co_{0.2})_2B_2N_{3-\delta}$	4.1(2)	0.56(5)
$La_3(Ni_{0.7}Co_{0.3})_2B_2N_{3-\delta}$	~3.8	⩽0.47
$La_3(Ni_{0.9}Cu_{0.1})_2B_2N_{3-\delta}$	6.0(2)	0.75(5)

Band structure calculations by Mattheiss,[20] Singh and Pickett[24] revealed for $La_3Ni_2B_2N_3$ that essentially two band manifolds contribute to $N(E_f)$: broad (dispersive) Ni-B-N s-p bands and relatively narrow (flat) Ni-3d bands. While Ni/Co(Cu) substitution may hardly effect the s-p manifold, there is a shift of the Fermi level E_f relative to the

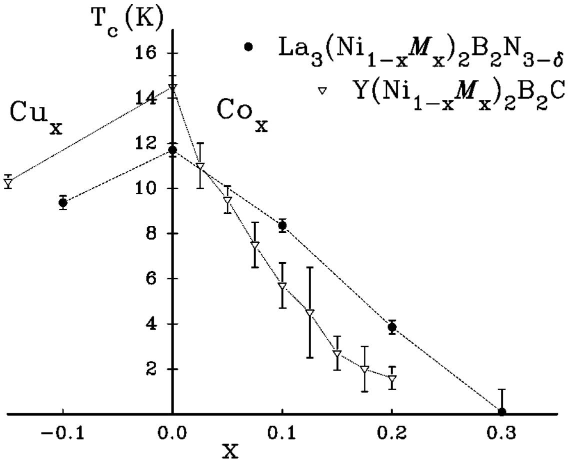

FIG. 6. Comparison of the T_c variation in $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$ and $Y(Ni_{1-x}M_x)_2B_2C$ (M=Co, Cu). The data of the latter are taken from Refs. 7, 8.

Ni/Co(Cu)-3d bands. The above reports[20,24] further suggest that the Fermi level of $La_3Ni_2B_2N_3$ lies at (or close to) a local maximum of $N(E)$. Hence, in a simple rigid band picture Ni/Co (Ni/Cu) substitution is expected to reduce (raise) the Fermi energy E_f relative to this local maximum, i.e., the calculated shape of $N(E)$ implies a reduction of $N(E_f)$ for Ni/Co and (less pronounced) for Ni/Cu substitution which is in agreement with the experimental results summarized in Table IV.

Concerning the structurally related borocarbides we pointed out in the introduction that Ni-site substitution studies on the ‘‘*single layer*’’ superconductors[5–8] YNi_2B_2C and $LuNi_2B_2C$ revealed a pronounced reduction of T_c (see Fig. 6 for a comparison of the T_c variation in the borocarbides and boronitrides). On the other hand in the case of normal conducting ‘‘*two layer*’’ YNiBC superconductivity up to 8 K could be induced by Ni/Cu substitution.[9] Hence, Cu substitution in the *single*- and *two-layer* borocarbides yields opposite effects upon T_c. In the scope of the rigid band argument, however, these effects are well in line with the band structure results[25] which suggest that the Fermi level of $Y(Lu)Ni_2B_2C$ coincides with a narrow peak in the density of states with $N(E_f)\sim 4$ states/(eV cell), while in the case of Y(Lu)NiBC E_f is situated below the corresponding maximum and $N(E_f)$ is just about 1.2 states/(eV cell), i.e., a shift of the Fermi level out of the EDOS maximum (minimum) goes in hand with a decrease (raise) of the transition temperature which is clearly observed in the corresponding experiments on $Y(Ni/Co, Cu)_2B_2C$ and Y(Ni/Cu)BC as well as in the present study on the nitrides.

For the borocarbides susceptibility studies[5,8] and a combined specific heat and susceptibility investigation[7] of the Ni-site substitution effect were reported with the conclusion that the suppression of superconductivity upon Co doping can primarily be traced back to the reduction of $N(E_f)$ and a (minor) change of Θ_D^{LT}. Thus it is obvious that the effect of Ni/Co substitution, in particular the mechanism which leads to the suppression of superconductivity in $Y(Ni_{1-x}Co_x)_2B_2C$ and $La_3(Ni_{1-x}Co_x)_2B_2N_{3-\delta}$ is rather similar, i.e., primarily governed by the reduction of the EDOS at the Fermi level. From the variation of the enhanced Pauli susceptibility $S\chi_{\mathrm{Pauli}}$ and the asymmetry of T_c as a function of the Co and Cu concentration in the borocarbides (see Fig. 6) it was argued by Gangopadhyay and Schilling[8] that the Stoner enhancement factor $S=1/[1-IN(E_f)]$ should be larger for Cu than for Co substitution, if the intra-atomic exchange I is the same in both systems. However, they found that for a given value of $SN(E_f)$ the Cu substituted compounds have a significantly higher T_c than those with Co indicative for a stronger electron phonon coupling in the former. To disentangle the influence of the Stoner enhancement and the electron-phonon coupling strength we use the results of the heat capacity measurements to analyze the susceptibility data.

The weak temperature dependent ‘‘Stoner Wohlfarth’’ susceptibility $\chi_0(1+aT^2)$ obtained from the fit including a Curie Weiss law contains contributions from the core diamagnetism, the Landau diamagnetism and the enhanced Pauli paramagnetism

$$\chi_0(T=0)=\chi_{\mathrm{core}}+\chi_{\mathrm{Landau}}+S\chi_{\mathrm{Pauli}} \tag{4}$$

with $\chi_{\mathrm{Pauli}}=\mu_B^2N(E_f)$ and $\chi_{\mathrm{Landau}}=-\mu_B^2N(E_f)/3(1+\lambda)^2$. The value for χ_{core} is estimated using the data of Ref. 26 to be -1.42×10^{-7} emu/g. Hence, one expects that χ_0 varies in a similar way as $N(E_f)$ as a function of the Ni/Co substitution which is indeed observed for the borocarbides by Hoellwarth *et al.*[7] However, the opposite trend is observed here in the boronitrides indicating that the Stoner enhancement factor grows with rising Co content for $x>0.1$. The relations above allow the evaluation of the Stoner enhancement factor

$$S=\frac{\chi_0-\chi_{\mathrm{core}}}{\mu_B^2N(E_f)}+\frac{1}{3(1+\lambda)^2} \tag{5}$$

using the data for λ and the bare density of states $N(E_f)$ given in Table IV. With the Stoner factor we further obtain an (average) value for the intra-atomic exchange I related to one unit cell. The results are listed in Table V together with the experimental values of χ_0 and the effective moments μ_{eff}, derived from the Curie constant. It is worth noting that the effective moments are of the same magnitude as those observed in the borocarbides and appear to be rather independent of the Co content while that of the Cu sample is by a factor of 2 larger. The latter can be associated with the reduced solubility range of Cu—as mentioned above—giving rise to a larger impurity content. On the other hand for both the Co and Cu samples with $x=0.1$ the value of χ_0 is slightly reduced as expected but increases for $x>0.1$ yielding growing Stoner enhancement factors.

The reanalysis of the susceptibility and specific heat data of Hoellwarth *et al.*[7] taking into account the Stoner enhancement by the same procedure as above gives also slightly increasing S values for $Y(Ni_{1-x}Co_x)_2B_2C$ ($S_{x=0}=1.7$, $S_{x=0.1}=1.8$, and $S_{x=0.2}=1.9$). Note the S value of the parent compound is in fair agreement with bandstructure calculations[27,28] ($S=1.3$–1.78). For a given intra-atomic exchange I the Stoner enhancement $S=1/[1-IN(E_f)]$ should decrease with falling $N(E_f)$, in contrast to the observation for $Y(Ni_{1-x}Co_x)_2B_2C$ and $La_3(Ni_{1-x}Co_x)_2B_2N_{3-\delta}$, thus we have to conclude that an enhanced intra-atomic exchange I is

TABLE V. Comparison of the experimental values of χ_0 with the Pauli susceptibility χ_{Pauli}, corresponding to the bare density of states $N(E_f)$, yielding the Stoner factor S and the intra-atomic exchange I of $La_3(Ni_{1-x}M_x)_2B_2N_{3-\delta}$. The μ_{eff} values account for contributions of paramagnetic impurities.

M_x	μ_{eff} (μ_B/f.u.)	χ_0	χ_{Pauli}	S	I (eV)
		($\times 10^{-7}$ emu/g)			
	0.18	4.35(5)	3.25	1.9	0.08
$Co_{0.1}$	0.14	4.10(5)	2.76	2.1	0.10
$Co_{0.2}$	0.17	4.81(5)	2.22	2.9	0.16
$Co_{0.3}$	0.14	5.40(5)	~ 2.06	~ 3.5	~ 0.19
$Cu_{0.1}$	0.33	4.14(9)	3.25	1.8	0.07

responsible for the increase of S with growing Co content as demonstrated by the I values given in Table V. The comparison of dS/dx_{Co} of the boronitride and the borocarbide system shows that the increase of S is damped by the stronger decrease of $N(E_f)$ in the latter, because $I \sim 0.08$ eV for both $La_3Ni_2B_2N_{3-\delta}$ and YNi_2B_2C and increases by $\Delta I/\Delta x \simeq 4$ meV/(mol % Co) for $La_3(Ni_{0.8}Co_{0.4})_2B_2N_{3-\delta}$ and $\Delta I/\Delta x \simeq 6$ meV/(mol % Co) for $Y(Ni_{0.8}Co_{0.4})_2B_2C$ [$N(E_f)$ taken from Ref. 7]. Of course, in the case of Cu substitution the intra-atomic exchange and in consequence the Stoner enhancement of the Pauli susceptibility should be weakened, because of filling up the d band.

The analysis of the correlations between T_c, $N(E_f)$, and λ of the $La_3(Ni_{1-x}Co_x)_2B_2N_{3-\delta}$ series clearly shows that magnetic pair-breaking effects do not play a role, because their contribution to the suppression of superconductivity would be in addition to the effect of the reduction of $N(E_f)$ and the concomitant decrease of the coupling strength λ which is already sufficient to explain the total reduction of T_c. Hence, the increase of the Stoner enhancement does not give rise to the appearance of magnetic fluctuations at least up to $x \leqslant 0.3$ and the asymmetry between the reduction of T_c and the Pauli susceptibility of $Y(Ni_{1-x}M_x)_2B_2C$ (M = Co, Cu; see Ref. 8) has to be attributed to a decrease of the Stoner enhancement on the Cu side rather than to occurrence of pair breaking on the Co side.

The comparison of the effect of Ni-site substitution by Co and Cu in $La_3Ni_2B_2N_{3-\delta}$ and YNi_2B_2C, in particular the similarity of $\Delta I/\Delta x$ and $\Delta N(E_f)/\Delta x \sim -0.10$ states/(eV f.u. mol % Co) for the nitride very close to -0.13 states/(eV f.u. mol % Co) for the borocarbides,[7] indicates that the electronic properties (band structure related to d electrons) of the Ni_2B_2 layers is more or less the same in both systems. The significantly higher T_c values of the borocarbides (e.g., 16 K of $LuNi_2B_2C$) have to be attributed to the stronger electron-phonon coupling due to soft phonons[29] rather than to a higher density of states (per atom). Note, the bare density of states $N(E_f)$ of $LaPt_{1.5}Au_{0.5}B_2C$ with $T_c \sim 11$ K as in the boronitride is just about 1.3 states/eV f.u. but despite of its much lower density of states this borocarbide superconductor has a higher $\lambda \simeq 1.1$ arising from very soft phonon modes (see Ref. 30). In the case of the boronitride the corresponding (soft) optical phonon branch is shifted to higher energies and $La_3Ni_2B_2N_{3-\delta}$ behaves as a weak-coupling superconductor[4] although its T_c is slightly higher than that of the ‘‘strong-coupling’’ superconductor $LaPt_{1.5}Au_{0.5}B_2C$.

V. CONCLUSION

In the $La_3(Ni_{1-x}Co_x)_2B_2N_{3-\delta}$ system single-phase samples were obtained for the substitution range $x = 0-0.3$ wherein superconductivity is gradually suppressed to below 1.5 K. Heat capacity measurements show that Ni/Co substitution (hole doping) causes a reduction of the Sommerfeld value γ, which is traced back to a decrease of the bare density of states $N(E_f)$ and a corresponding fall of the coupling strength λ. From the combined analysis of the susceptibility and heat capacity results we further evaluated the Stoner enhancement of the Pauli susceptibility which raises with the Co content, because an enhancement of the intra-atomic exchange I overcompensates the reduction of $N(E_f)$. Nevertheless, our results show that the decrease of T_c is primarily related to the reduction of $N(E_f)$ and the corresponding decrease of λ, while there is no hint for the occurrence of magnetic fluctuations which could be accompanied by pair-breaking effects.

Electron doping in $La_3(Ni_{1-x}Cu_x)_2B_2N_{3-\delta}$ with a reduced solubility range ($0 < x_{\mathrm{Cu}} \leqslant 0.1$) results in a modest depression of the superconducting transition $dT_c/dx \simeq -23$ mK/(mol % Cu). Attempts to replace Ni by the 4d or 5d metals Pd and Pt yielded multiphase samples which behave as normal metals down to 4.2 K.

The above results are in line with available bandstructure calculations for $La_3Ni_2B_2N_3$ which suggested the Fermi level to be at a maximum of the electronic density of states. Hence, the possibility of raising T_c by transition metal substitutions appears to be rather unlikely.

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