Physical properties and electronic structure of La_3Co and La_3Ni intermetallic superconductors

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Abstract

La_3Co and La_3Ni are reported superconductors with transition temperatures of 4.5 and 6 K, respectively. Here, we reinvestigate the physical properties of these two intermetallic compounds with magnetic susceptibility χ , specific heat C_p and electrical resistivity ρ down to 1.9 K. Although bulk superconductivity is confirmed in La_3Co , as observed previously, only trace superconductivity is found in La_3Ni , indicating that the superconductivity in La_3Ni originates from an impurity phase. Superconducting state parameters for La_3Co , including lower and upper critical fields and the superconducting gap, are estimated. Results of the theoretical calculations of the electronic structure for both materials are also presented, and comparison of the Fermi level location in La_3Co versus La_3Ni explains its larger superconducting T_c . A major discrepancy between band structure calculations and the experimentally measured Sommerfeld coefficient is found. The measured electronic density of states is about 2.5 times larger than the theoretical value for La_3Co . This effect cannot be explained by the electron-phonon interaction alone. This renormalization of g , as well as an $\sim T^2$ behavior of the resistivity, suggests the presence of spin fluctuations in both systems.

Keywords: superconductivity, intermetallic compounds, band structure calculations

I. Introduction

RE_3M binary intermetallics, where RE is a rare earth metal and $M = \text{Co}$ or Ni , belong to a large family of compounds which crystallize in the orthorhombic crystal structure with space group $Pnma$ (s.g. #62, Pearson symbol $oP16$). A prototype of this structure is an iron carbide known as cementite with the chemical formula Fe_3C . Its characteristic feature are trigonal prisms that are formed by iron atoms and centered by a carbon atom (see Fig. 1). Cementite has been studied for decades and remains an important field of study [1][2].

Fig. 1 Unit cell of cementite-type La_3Co intermetallic compound. Cobalt atoms (blue) at $4c$ site are surrounded by lanthanum atoms (green) from $8d$ and $4c$ positions, forming trigonal prisms.

Electrical and magnetic properties [3][4] as well as specific heat [5] of several RE_3Co binary compounds have been studied in details. Neutron diffraction studies on Dy_3Co [6] and Er_3M ($M=\text{Co}, \text{Ni}$) [7] show that only RE atoms carry a magnetic moment whereas Co and Ni atoms remain non-magnetic. Therefore replacing a magnetic lanthanide by lanthanum in RE_3M should lead to paramagnetic behavior and since there is a high concentration of La one can naively expect the presence of superconductivity. Indeed, C. S. Garde, *et al.* reported superconductivity in the La_3M series for various M metals including Ni and Co [8]. The highest superconducting critical temperature, estimated from resistivity measurements, was reported for La_3In ($T_c = 9.7 \text{ K}$) and T_c of approximately 6 K was estimated for as many as four compounds: La_3Ga , La_3Sn , La_3Al and La_3Ni .

The most intriguing superconductors in the La_3M family are La_3Co and La_3Ni . Superconductivity in Co and Ni containing compounds is rather rare due to the strong magnetic character of Co and Ni atoms, that might break the Cooper pairs and destroy superconductivity. Fisk and Lawson reported superconductivity in La_3Co with $T_c = 4.3$ K [9], and more detailed studies, including electrical resistivity, magnetic susceptibility, heat capacity and thermopower, were performed later [10], [11], [12]. An intriguing feature of the resistivity data for La_3Co and La_3Ni is a $\rho(T) \sim AT^2$ dependence below 20 K, characteristic of Fermi-liquid behavior. From the resistivity and the heat capacity data, Lu, *et al.* calculated a Kadowaki-Woods ratio for La_3Co and obtained a value of $A/\gamma^2 = 0.46 \cdot 10^{-6} \Omega \text{ m (K mol / J)}^2$ that is close to the “universal” value of $10^{-7} \Omega \text{ m (K mol / J)}^2$ observed in heavy-fermion compounds [11]. A slightly lower value $A/\gamma^2 = 0.28 \cdot 10^{-6} \Omega \text{ m (K mol / J)}^2$ was found for La_3Ni [13]. The latter compound was claimed to be an unconventional superconductor with $T_c \sim 1.45$ K, based on heat capacity measurements [14], [13]. However, a second heat capacity peak in samples that are nominally La_3Ni at $T \sim 2.4$ K [14] is likely caused by a La_7Ni_3 impurity phase [15], and, therefore, the unconventional character of La_3Ni is questionable.

The aim of this article is to present details of the superconducting properties of binary intermetallic La_3Co superconductor, compare them with La_3Ni , and analyze in view of the bandstructure calculations. Measurements of magnetization, specific heat and transport properties confirm bulk superconductivity of La_3Co , and in contrast only filamentary superconductivity is observed for La_3Ni .

The paper is structured as follows. In section II the experimental details are provided. The electrical resistivity, magnetic susceptibility and heat capacity data for La_3Co and La_3Ni are given in section IIIA and section IIIB, respectively. We provide superconducting parameters for La_3Co and compare the normal state parameters for La_3Co and La_3Ni . In section IV we discuss the band structure calculations for both compounds and we conclude in section V.

II. Experimental

Polycrystalline samples of La_3Co and La_3Ni were synthesized by arc-melting stoichiometric amounts of lanthanum (99.9%) and cobalt (99.95%) or nickel (99.95%), respectively. Melting took place under ultra-high purity argon atmosphere, in a water-cooled copper hearth. We used tungsten as the electrode material, and a zirconium button was used as an oxygen getter. The samples were re-melted four times to get homogeneous materials. The arc-melted buttons

were wrapped in tantalum foil, placed in evacuated quartz tubes and annealed at 500°C for two weeks. The phase purity of samples was checked by powder x-ray diffraction (XRD) on a PANalytical X'Pert Pro diffractometer with a Cu K_α source. PowderCell software was used for XRD pattern simulation [16].

All measurements of physical properties were performed by using a Quantum Design Physical Properties Measuring System PPMS-9. For La_3Co the isothermal magnetization and temperature dependence of the *dc* magnetic susceptibility were measured. Furthermore, the temperature dependence of the *ac* magnetization was measured on both compounds in a *dc* field of 5 Oe and 1 kHz excitations with an amplitude of 3 Oe. The specific heat measurements were performed using a standard relaxation method between 1.9 and 300 K at 0 and 3 T magnetic field. The electrical resistivity measurements were carried out by the standard four-probe method with 50 μm diameter platinum wires spot-welded to the samples.

III. Results

A. Powder x-ray diffraction

XRD patterns measured on powdered samples are shown in Supplementary material Fig. S1 and Fig. S2. As both samples oxidize quickly in air only short XRD scans could be performed. The obtained XRD patterns match the diffraction patterns of La_3Co and La_3Ni (Refs. [8] and [17], [18] respectively). A large number of observed diffraction reflections results from low symmetry of cementite-type structure. There are some reflections from unrecognized phase observed for both samples, most probably arising from minor amounts of β -lanthanum or lanthanum oxides.

B. Physical properties of La_3Co

The temperature dependence of the normal-state resistivity $\rho(T)$ of La_3Co between 1.9 K and 300 K at $H = 0$ is presented in the main panel of Fig. 2. The resistivity data display metallic-like character ($d\rho/dT > 0$). The residual resistivity (ρ_0) estimated at $T = 4.7$ K before entering the superconducting state is 43 $\mu\Omega\text{ cm}$ and the residual resistivity ratio ($\text{RRR} \equiv \rho_{300\text{ K}}/\rho_0$) is 6. An inset of Fig. 2 presents the zero-field-cooled (ZFC) and field-cooled (FC) *dc* volume magnetic susceptibility data $\chi(T)$ in the vicinity of the superconducting transition. The diamagnetic response was normalized by a demagnetization factor that was estimated from isothermal magnetization measurements $M(H)$ in the superconducting state and will be

described later. The superconducting critical temperature (T_c) was taken as the temperature where the extrapolation of the normal state susceptibility to lower temperatures intersects the extrapolation of the steepest slope of the $\chi(T)$ curve [19]. The T_c found for La_3Co in these measurements is 4.3 K, which is close to the previously reported values [9]. The much weaker FC signal indicates a significant pinning effect on grain boundaries.

Fig. 2 Main panel: temperature dependence of resistivity showing the superconducting transition at 4.6 K. Inset shows the magnetic susceptibility versus temperature, observed in zero-field-cooling (ZFC) and field-cooling (FC) modes. The magnetic field was 10 Oe and the estimated superconducting critical temperature is 4.27 K.

To highlight the superconducting transition, the low temperature resistivity curves $\rho(T)$, under applied magnetic fields from 0 T to 3 T with a step of 0.2 T, are shown in the main panel of Fig. 3. In the zero-field data, a sudden drop of resistivity is observed below ~ 6 K, but the transition is not complete. Another drop is seen below 5 K, finally reaching a zero resistance state at 4.6 K. This behavior is likely caused by a small fraction of unreacted β -lanthanum (fcc type) with $T_c = 5.95$ K [20]. β -La has a critical field of ~ 0.11 T [21] and therefore at higher fields the measured superconducting transition becomes sharp and is representative of La_3Co with a width of 10 mK estimated for $\mu_0 H = 0.6$ T. Above 2 T, a two step transition is seen again, and for the highest magnetic field applied (3T) $T_{c \text{ onset}}$ is about 2.3 K (marked by a vertical arrow). The origin of this behavior is unclear, although, it might originate from the presence of an unknown impurity phase, which superconducts with a rather large upper

critical field. From our $\rho(T)$ measurement we conclude that the zero-field T_c for La_3Co is just above 4.6 K, the temperature at which the transition is complete.

In the inset of Fig. 3, the upper critical field determined from the resistivity measurements for La_3Co is plotted. The orbital critical field, for a one-band BCS-type superconductor, can be calculated from the Werthamer-Helfand-Hohenberg expression: $H_{c2}(T) = -AT_c \frac{dH_{c2}}{dT} \Big|_{(T=T_c)}$ where A is 0.69 and 0.73 in the dirty and clean limits, respectively [22]. The slope of $H_{c2}(T)$ close to T_c is $dH_{c2}/dT = -1.1 \text{ T/K}$ and using $T_c = 4.6 \text{ K}$, we found $\mu_0 H_{c2}(0) = 3.5 \text{ T}$ in the dirty and 3.7 T in the clean limit. The value of upper critical field is about half of the Pauli paramagnetic limit [23] of $\mu_0 H^p_{c2} = 1.84T_c = 6.44 \text{ T}$, which suggests the orbital pair breaking mechanism is dominant.

Fig. 3 La_3Co . Main panel: the superconducting transition under various magnetic fields. Inset: the upper critical field as determined by the temperature at which the resistance drops to 50% of ρ_0 . The red solid line is the best fit to the formula $H_{c2}(T) = H_{c2}(0)[1 - (T/T_c)^n]$.

An alternative estimation of the upper critical field is possible by using an empirical power law expression: $H_{c2}(T) = H_{c2}(0)[1 - (T/T_c)^n]$. A least square fit to the $H_{c2}(T)$ data is represented by a red line in the inset of Fig. 2, and yields $\mu_0 H_{c2}(0) = 4.1(1) \text{ T}$, $T_c = 4.6(1) \text{ K}$ and $n = 1.31(4)$. For further calculations we take upper critical field $\mu_0 H_{c2}(0) = 4.1 \text{ T}$. This value is twice larger than reported in ref. [10].

Assuming that the upper critical field is determined by orbital pair breaking, the superconducting coherence length ξ_{GL} can be calculated from the Ginzburg-Landau relation $\xi_{GL}(0) = \{\phi_0/[2\pi H_{c2}(0)]\}^{1/2}$, where $\phi_0 = h/2e$ is the quantum of magnetic flux. For La_3Co we obtain $\xi_{GL}(0) = 9$ nm, which is comparable to $\xi_{GL} = 13$ nm estimated for the Heusler compound HfPd_2Al ($T_c \sim 3.5$ K) [24] and much shorter than $\xi_{GL} = 55$ nm calculated for $\beta\text{-La}$ [21].

The superconducting state is further characterized by the isothermal magnetization versus magnetic field measurements and the results are shown in Fig. 4 (a). The initial slope of the volume magnetization dM_V/dH is larger than $-1/4\pi$, indicating a nonzero demagnetization factor. Assuming that the linear response to a magnetic field is perfectly diamagnetic, we obtain a demagnetization factor $d = 0.3$ that is consistent with the sample shape. Fig. 4 (b) shows the difference between magnetization $M_V(H)$ and a fit to the data (M_{dia}) in the low-field range where the $M_V(H)$ function is linear. The magnetic field for which $M(H)$ starts to differ from M_{dia} is the lower critical field H_{c1} . Those values are plotted as a function of temperature (see Fig. 4 (c)) and then fit to the formula $H_{c1}(T) = H_{c1}^*(0)[1 - (T/T_c)^2]$. From this fit we obtain $H_{c1}^*(0) = 130$ Oe and taking the demagnetization factor $d = 0.3$, the lower critical field for La_3Co is estimated to be $H_{c1}(0) = H_{c1}^*(0)/(1 - d) = 186$ Oe. This value is five times lower than $H_{c1}(0) = 1$ kOe reported for La_3Co in ref. [10], which was obtained by assigning H_{c1} to the minimum of the $M(H)$ curves.

Fig. 4 (a) Magnetization versus magnetic field at various temperatures. The solid red line shows the fit to the 2 K data in the low- H range where a linear $M(H)$ dependence is observed. (b) Difference between the measured magnetization and a perfect diamagnetic response (M_{dia}) in the 2 – 4 K temperature range. (c) Lower critical field, determined by when the magnetization deviates by 10% from perfect diamagnetism, versus temperature. To estimate $\mu_0 H_{c1}(0)$, the data are fit using the formula $H_{c1}(T) = H_{c1}(0)[1 - (T/T_c)^2]$ (red solid line).

A Ginzburg-Landau superconducting penetration depth is calculated from the relation $\mu_0 H_{c1} = \frac{\Phi_0}{4\pi\lambda_{\text{GL}}^2} \ln \frac{\lambda_{\text{GL}}}{\xi_{\text{GL}}}$ and we obtain $\lambda_{\text{GL}}(0) = 160$ nm. Taking this value we get the Ginzburg-Landau parameter $\kappa = \lambda_{\text{GL}}(0)/\xi_{\text{GL}}(0) = 18$, and hence La_3Co is a type-II superconductor. The thermodynamic critical field $H_c(0) = 1480$ Oe is estimated from the relation $H_{c1}H_{c2} = H_c^2 \ln(\kappa)$.

The overall temperature dependence of the specific heat (C_p) is presented in Fig. 5 (a). The normal state C_p measured at room temperature and in zero magnetic field is close to the expected classical Dulong-Petit high-temperature limiting value ($C = 3nR = 99.8$ J mol⁻¹ K⁻¹, where $n = 4$ is the number of atoms per formula unit and $R = 8.314$ J mol⁻¹ K⁻¹ is the gas constant). Fig. 5 (b) presents the variation of C_p/T with T^2 in the temperature range from 1.9 K to 5.5 K at a magnetic field of $\mu_0 H = 3$ T. The experimental data points are fit using the formula $C_p/T = \gamma + \beta T^2 + \delta T^4$, where the first term (γT) is the electronic contribution to the specific heat, and the second (βT^3) and third (δT^5) terms are contributions from the lattice.

The fit provides values of the Sommerfeld coefficient $\gamma = 31.8(2) \text{ mJ mol}^{-1} \text{ K}^{-2}$, $\beta = 3.18(3) \text{ mJ mol}^{-1} \text{ K}^{-4}$, and $\delta = 5(1) \mu\text{J mol}^{-1} \text{ K}^{-6}$.

Fig. 5 (a) The plot of heat capacity versus temperature. Measured data are represented by open circles, and the solid red line is a fit to a model where 86% of the weight is given by the Debye model (blue line) and the remaining weight comes from an the Einstein mode (green line). (b) C_p/T versus T^2 . Solid blue line is a fit to $C_p/T = \gamma + \beta T^2 + \delta T^4$ in the low-temperature region. (c) C_{el}/T ($= C_p/T - \beta T^2 + \delta T^4$) as a function of temperature measured in zero field. Solid line represents the theoretical temperature-dependence from a spin-singlet fully gapped superconductor according to weak coupling BCS theory.

Using a simple Debye model for the lattice contribution, we estimated the Debye temperature Θ_D from the relation $\Theta_D = \left(\frac{12\pi^4}{5\beta} nR \right)^{1/3}$. The calculated Debye temperature is 135 K, which corresponds to the fact that the examined compound mostly consists of heavy elements (lanthanum). It is worth noting that for pure La the reported value of the Debye temperature is 142 K [25]. The Sommerfeld coefficient and the Debye temperature are in reasonable agreement with the values provided by Sato, *et al.* $\gamma = 26 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\Theta_D = 127 \text{ K}$ [10].

A pure Debye model with $\Theta_D = 135 \text{ K}$ is insufficient to explain the experimental heat capacity data above 50 K. This suggests that higher energy optical modes must play a significant role

in the heat capacity data at higher temperatures, and, therefore, we fit the data in the whole temperature range with the formula: $C_p = \gamma T + k C_{\text{Debye}}(T) + (1 - k) C_{\text{Einstein}}(T)$. The first term (γT) corresponds to the electronic contribution, the k parameter represents the weight of the phonon contributions to the specific heat given by the Debye (C_{Debye}) and Einstein (C_{Einstein}) models, respectively:

$$C_{\text{Debye}}(T) = 9nR \left(\frac{T}{\Theta_D} \right)^3 \int \frac{x^4 \exp(x)}{[\exp(x)-1]^2},$$

$$C_{\text{Einstein}}(T) = 3nR \left(\frac{\Theta_E}{T} \right)^2 \exp \left(\frac{\Theta_E}{T} \right) \left[\exp \left(\frac{\Theta_E}{T} \right) - 1 \right]^{-2},$$

where Θ_E is the Einstein temperature.

The fit, represented by the solid red line in Fig. 4 (a), possesses an 86 % contributions from the Debye mode, and the remaining weight comes from an Einstein mode with $\Theta_E = 302(12)$ K. The determined $\Theta_D = 131(1)$ K is close to temperature derived from the low temperature fit shown in Fig 4 (b).

The electron-phonon coupling constant is estimated from the inverted McMillan formula [26]:

$$\lambda_{ep} = \frac{1.04 + \mu^* \ln \left(\frac{\Theta_D}{1.45 T_c} \right)}{(1 - 0.62 \mu^*) \ln \left(\frac{\Theta_D}{1.45 T_c} \right) - 1.04},$$

where μ^* is the Coulomb repulsion constant, which typically has a value between 0.1 and 0.15. In this case, we assume $\mu^* = 0.13$. So, taking $T_c = 4.57$ K and $\Theta_D = 135$ K, we calculated the electron-phonon coupling constant $\lambda_{ep} = 0.82$.

From the temperature dependence of the electronic specific heat capacity (C_{el}) below T_c (Fig. 5 (c)) we extract a value for the superconducting gap by fitting the data to generalised weak-coupling BCS expectation:

$$C_{BCS} = t \frac{d}{dT} \int_0^\infty dy \left(\frac{-6\gamma\Delta_0}{k_B\pi} \right) [f \ln f + (1 - f) \ln(1 - f)],$$

where $t = T/T_c$, f is the Fermi function $f = 1/(e^{E/k_B T} + 1)$, $E = \sqrt{\varepsilon^2 + \Delta^2}$, $y = \varepsilon/\Delta(0)$, and $\Delta(T)/\Delta(0)$ is taken from the tabulated values of Mühlischlegel [27]. The good agreement of the fit suggests that La_3Co is a fully gapped spin-singlet BCS superconductor with $\Delta(0) = 0.74$ meV.

The superconducting transition, seen as an abrupt jump in C_{el}/T is observed at 4.5 K, is consistent with the result from the resistivity data. Having the magnitude of the anomaly $\Delta C_{el}/T_c$ and the Sommerfeld parameter γ we calculate $\Delta C_{el}/\gamma T_c = 1.66$, which is more than the BCS value of 1.43 for a weakly coupled superconductor. This may indicate intermediate coupling in La_3Co .

Table 1 collects our measured and derived superconducting and normal state parameters for La_3Co .

Table 1. Superconducting and normal state parameters of La_3Co

Parameter	Unit	Value
T_c	K	4.57
$\mu_0 H_{c2}(0)$	T	4.1
$\mu_0 H_{c1}(0)$	mT	18.6
$\mu_0 H_c$	T	0.16
λ_{e-p}		0.83
$\xi_{GL}(0)$	nm	9
$\lambda_{GL}(0)$	nm	160
κ		18
γ	$\text{mJ mol}^{-1} \text{K}^{-2}$	31.8
β	$\text{mJ mol}^{-1} \text{K}^{-4}$	3.18
Θ_D	K	135
RRR		6
$\Delta C_p/k_B T$		1.83
Δ	meV	0.74

B. Physical properties of La_3Ni

Normal-state resistivity $\rho(T)$ of La_3Ni versus temperature in the range of 1.9 - 300 K, measured in $\mu_0 H = 0$ T, is presented in Fig. 6.

Fig. 6 Temperature dependence of resistivity for La_3Ni . The inset expands the same results in the temperature range from 1.9 to 3.5 K. Lower panel shows the result of the $\rho = \rho_0 + AT^2$ fit for both La_3Co and La_3Ni .

The resistivity of La_3Ni shows metallic-like character ($d\rho/dT > 0$) with a drop in $\rho(T)$ below ~ 2.2 K. The residual resistivity above the transition is $18 \mu\Omega\text{cm}$ and the residual resistivity

ratio $RRR = 8$. The inset of Fig. 6a shows the temperature dependence of resistivity near the transition to the superconducting state. The onset of the transition, occurring at about $T_{c \text{ onset}} = 2.2$ K, is in poor agreement with previous reports for La_3Ni ranging from $T_c = 6.2$ K [8] to 1.45 K [14]. The origin of this discrepancy is discussed later.

The lower panel of Fig. 6 presents low temperature $\rho(T)$ versus T^2 together with the fits to $\rho(T) = \rho_0 + AT^2$. The obtained values of $A = 0.028(1) \mu\Omega \text{ cm K}^{-2}$ for La_3Co and $A = 0.016(1) \mu\Omega \text{ cm K}^{-2}$ for La_3Ni , are in very good agreement with those reported in the literature [11] [13].

Fig. 7 Real part of the ac magnetization for La_3Ni (solid black circles) and La_3Co (open blue circles).

Temperature dependence of the real part of the *ac* magnetization for La_3Ni and La_3Co are presented in Fig. 7 from 1.8 to 7 K, which covers the resistively determined transition temperature for both samples. The measurements are conducted under low applied magnetic fields $H_{dc} = 5$ Oe and $H_{ac} = 3$ Oe, $f = 1$ kHz. A wide transition with a small diamagnetic signal is observed for La_3Ni . The transition temperature ($T_c = 2.2$ K) is in agreement with the T_c estimated from the resistivity measurement.

To shed more light on the physical properties of La_3Ni we measured the temperature dependence of the heat capacity (C_p). Fig. 8(a) presents temperature dependence of $C_p(T)$ in the temperature range of 1.9 – 300 K. At room temperature $C_p(300 \text{ K})$ value is in good agreement with the expected value from the classical Dulong-Petit law ($C = 3nR = 99.8 \text{ J mol}^{-1}$

¹ K⁻¹). Further analysis was performed as described for La₃Co. In particular, the combined Einstein and Debye models are used to fit the experimental C_p data, as illustrated by the solid red line in Fig. 6(a). The contribution of the Debye model with $\Theta_D = 126(3)$ is estimated to be 68 % of the weight, and the remaining weight comes from an Einstein mode with $\Theta_E = 180(7)$ K.

Fig. 8 Results of specific heat measurements on La₃Ni. (a) Specific heat vs. temperature over the entire investigated temperature range (1.9-300 K). The solid red line show a fit to the experimental data (black circles). (b) C_p/T versus T^2 . Solid blue line is a fit to $C_p/T = \gamma + \beta T^2 + \delta T^4$. (c) $C_{el.}/T$ ($= C_p/T - \beta T^2 + \delta T^4$) as a function of temperature measured in zero field. Solid line represents the minimum expected specific heat jump due to weak coupling superconductivity.

The Sommerfeld parameter and alternative value of the Debye temperature are obtained from the $C_p/T = \gamma + \beta T^2 + \delta T^4$ low temperature fit, presented in Fig. 8 (b). From this we obtained $\gamma = 16.7(3)$ mJ mol⁻¹ K⁻², $\beta = 1.82(2)$ mJ mol⁻¹ K⁻⁴ and $\delta = 9.8(1)$ μ J mol⁻¹ K⁻⁶. The calculated Debye temperature $\Theta_D = 162$ K is found to be slightly higher than we estimated for La₃Co (135 K). The Sommerfeld coefficient and the Debye temperature are close to the reported values of Sato, *et al.* $\gamma = 20.6$ mJ mol⁻¹ K⁻², $\Theta_D = 170$ K [14].

Fig. 8 (c) shows the temperature dependence of C_{el}/T and sheds light on superconductivity in La_3Ni . There is no clear anomaly observed in the electronic heat capacity above 1.9 K. Assuming La_3Ni is a superconductor with $T_c = 2.2$ K, as suggested by the magnetic and resistivity measurements, we expect an anomaly with $\Delta C_{el}/T \sim 20 \text{ mJ mol}^{-1} \text{ K}^{-2}$, estimated from the BCS relation $\Delta C_{el}/\gamma T = 1.43$. The lack of the specific heat jump for La_3Ni strongly suggests that La_3Ni does not superconduct above 1.9 K. The transition temperature, determined from resistivity and magnetization measurements, likely originates from the minority phase La_7Ni_3 for which the reported T_c is 2.1 K [15]. Bulk La_3Ni itself exhibits superconductivity only below 1.45 K [13].

IV Electronic structure

Electronic structure calculations for both La_3Co and La_3Ni were performed using the full potential Korringa-Kohn-Rostoker method [28]–[30], within the local density approximation (LDA) of Perdew and Wang [31]. Computations were done on a fine k-point mesh of about 2000 points in the Brillouin zone, with the angular momentum expansion up to $l_{max} = 3$. The experimental unit cell parameters and atomic positions [8], [32] were used in the computations, and are presented in Table 2. As was mentioned before, the unit cells of the studied compounds contain four formula units, with 16 atoms per unit cell, distributed among three inequivalent crystal sites, namely (8d) and (4c) for La, and (4c) for Co/Ni.

Table 2. Experimental unit cell parameters [8,29] of La_3Co and La_3Ni in the orthorhombic Pnma space group.

	La_3Co	La_3Ni
a (Å)	7.279	7.189
b (Å)	10.088	10.160
c (Å)	6.578	6.650
La(1) (8d)	(0.1688, 0.0685, 0.6727)	(0.18, 0.064, 0.18)
La(2) (4c)	(0.0461, 0.25, 0.1434)	(0.033, 0.25, 0.635)
Co/Ni (4c)	(0.3829, 0.25, 0.9396)	(0.391, 0.25, 0.436)

Both compounds, despite containing "magnetic" transition metal elements (Co, Ni), are reported to be paramagnetic. Our band structure calculations confirm this observation, i.e. in the spin-polarized computations magnetic moments on all the atoms converged to zero.

From here on, we discuss only non-magnetic calculations. Fig. 9 presents the energy dependent densities of states (DOS) of the studied materials, plotted per formula unit. On a broad scale, both compounds exhibit similar DOS profiles. Although La_3Ni contains one additional electron relative to La_3Co , the electronic structure is not a perfectly rigid shift between the two compounds. We can distinguish two characteristic features of the DOS. The first is the lower-lying transition metal $3d$ DOS maximum, located roughly -2 eV below the Fermi level (E_F), and the second, much larger DOS peak is associated with the empty $4f$ La electronic states, 2 eV above E_F . The Fermi level is located in between these two DOS peaks.

Fig. 9 Computed densities of states (DOS) of La_3Co (top panel) and La_3Ni (bottom panel). The total DOS (black solid line) is given per formula unit, whereas partial atomic densities are given per atom.

A zoom of the DOS near the Fermi level, as well as the angular momentum decomposition of the atomic densities of states, is shown in Fig. 10 for La_3Co and in Fig. 11 for La_3Ni . The zoom near E_F reveals the differences between the two compounds, which will be important for the superconductivity in the materials. In La_3Co , E_F is placed in a local DOS minimum, between two small peaks, with the total DOS value $N(E_F) = 5.2 \text{ eV}^{-1}$ per f.u. (see, Table 3). All the constituent atoms contribute equally to the DOS near E_F , if counted per single atom. The partial La DOS at E_F is formed mainly from its $5d$ orbitals, and the two inequivalent La(1) and La(2) atoms exhibit very similar DOS. Interestingly, as we already observed in Fig. 10, the $3d$ electronic states of Co are dominantly pushed below the chemical potential (-2 eV below E_F), and the $3d$ DOS at E_F is about $N_{3d\text{Co}}(E_F) = 0.63 \text{ eV}^{-1}$ per Co atom. This results in non-magnetic Co atoms in this compound, since the computed Stoner parameter for the d-shell is approximately 0.5, i.e. below the critical value of 1.0. The Co $4p$ orbitals' contribution to the DOS near E_F , is similar to the $3d$'s. On the other hand, La_3Ni , which has 1 valence electron per f.u. more than La_3Co (4 more per unit cell), has its E_F placed on the border of a deep DOS minimum, which is absent in La_3Co . In the rigid band picture adding one electron to the DOS of La_3Co , would cause E_F to jump to the next DOS valley, seen $\sim 0.2 \text{ eV}$ above E_F in Fig. 10. This valley, however, becomes much deeper in La_3Ni , resulting in a lower value of $N(E_F) = 4.1 \text{ eV}^{-1}$ per f.u. Assuming all other parameters remain the same, the reduction in $N(E_F)$ is a natural explanation for the lower superconducting transition temperature in La_3Ni relative to La_3Co . Comparing the DOS of Ni with that of Co, we also notice a larger filling of the $3d$ states, resulting in a lower $N_{3d\text{Ni}}(E_F) = 0.29 \text{ eV}^{-1}$ per Ni, being even smaller than the $4p$ DOS, $N_{4p\text{Ni}}(E_F) = 0.39 \text{ eV}^{-1}$ per Ni. This evolution of the electronic structure and different E_F location is also clearly seen in the electronic dispersion curves, plotted in Fig. 12. Firstly, the Fermi level in La_3Ni moves to the energy range, where there is a "gap" between electronic bands in some parts of the Brillouin zone for La_3Co (seen here in the Y-T-Z-U-X path). Secondly, additional "gaps" open, when Co is substituted with Ni (see X- Γ and Z-Y directions for example). All these lead to the formation of the deep DOS minimum near E_F for La_3Ni .

Fig. 10 La_3Co . (a) Total DOS (black solid line) and atomic partial DOS (in colors) near the Fermi level. (b-d) Angular momentum decomposition (in colors) of the atomic partial DOS (solid black lines).

Fig. 11 La_3Ni . (a) Total DOS (black solid line) and atomic partial DOS (in colors) near the Fermi level. (b-d) Angular momentum decomposition (in colors) of the atomic partial DOS (solid black lines).

Fig. 12 Electronic dispersion relations in La₃Co (left) and La₃Ni (right). The Brillouin zone, with the high symmetry points, is presented in the middle. The arrow shows the approximate location of the La₃Ni Fermi level, with regard to La₃Co.

The presented results suggest that the difference in superconducting transition temperatures between La₃Co (4.6 K) and La₃Ni (1.45 K) is primarily due to the differences in the electronic structure and the relatively unfavorable position of the Fermi level in La₃Ni.

Table 3. Densities of states at the Fermi level

	$N(E_F)$ (eV ⁻¹)
La ₃ Co	5.21
La(1)	1.32
La(2)	1.36
Co	1.21
La ₃ Ni	4.10
La(1)	1.09
La(2)	1.17
Ni	0.77

Our theoretical results seem to consistently describe the differences in the electronic structure and superconductivity between La₃Co and La₃Ni. There is, however, one major problem, which shows that these materials may be more complicated than initially expected. The comparison of the computed and measured electronic specific heat coefficient γ reveals that the measured values are considerably higher than expected (see, Table 3). If we assume, that the band structure value of γ_{calc} is renormalized only by the electron-phonon interaction, i.e. $\gamma_{expt} = \gamma_{calc}(1 + \lambda)$, this would lead to very large $\lambda = 1.59$ for La₃Co and larger than expected $\lambda = 0.77$ for La₃Ni. Such large values of λ do not correspond to the observed critical temperature values. Using the standard McMillan formula, measured Debye and critical temperatures and a Coulomb pseudopotential value $\mu^* = 0.13$ (see, also Section III) would give $\lambda = 0.82$ for La₃Co and $\lambda = 0.54$ for La₃Ni. The discrepancy for La₃Ni is small; however, the value for La₃Co is almost two times larger than the McMillan's formula predicts, which is

not a very common situation. Alternatively, if the λ values estimated from the γ parameters are used to calculate T_c , transition temperatures as large as 12 K for La_3Co and 4 K for La_3Ni are obtained (see, $T_{c,0}$ values in Table 4).

Table 4. Analysis of the electronic specific heat, electron-phonon coupling constant and critical temperatures for the bare values of λ and renormalized by the spin fluctuations.

	La_3Ni	La_3Co
$\Theta_{\text{D expt}}$ (K)	162	135
γ_{expt} (mJ/mol K ²)	16.7	31.8
γ_{calc} (mJ/mol K ²)	9.66	12.28
$\lambda_0 = \gamma_{\text{expt}}/\gamma_{\text{calc}} - 1$	0.729	1.590
$T_{c,0}$ ($\mu^* = 0.13$) (K)	4.00	12.32
λ_{sf}	0.055	0.170
$\lambda_{\text{ph}} = \lambda_0 - \lambda_{\text{sf}}$	0.674	1.420
μ_{eff}^*	0.175	0.256
λ_{eff}	0.639	1.213
$T_{c, \text{eff}}$ (K)	1.48	4.58
$T_{c, \text{expt}}$ (K)	1.45	4.57

To bring the T_c down to the measured values, one would need to apply a very large value of the Coulomb pseudopotential parameter $\mu^* = 0.22$ for La_3Ni and $\mu^* = 0.35$ for La_3Co , far above the commonly accepted level of $\mu^* = 0.10 - 0.15$, applied for most intermetallic superconductors. This renormalization of the Sommerfeld parameter, as well as the quadratic temperature dependence of the resistivity, suggests that spin fluctuations may be present in these materials. Similar discrepancy of the bandstructure γ_{calc} and experimental γ_{expt} values, most likely due to spin fluctuations, accompanied by the T^2 -dependence of resistivity, were reported for paramagnetic Co-based Laves phases, as YCo_2 [33] or LuCo_2 [34].

In such a case of a superconductor with spin fluctuations, the Sommerfeld parameter is renormalized both by the electron-phonon λ_{ep} and electron-paramagnon λ_{sf} ("spin fluctuations") interaction parameters: $\gamma_{\text{expt}} = \gamma_{\text{calc}}(1 + \lambda_{\text{ep}} + \lambda_{\text{sf}})$. The presence of paramagnons compete with superconductivity, and the effect on T_c may be estimated, using the McMillan formula with the renormalized values of μ^* and λ . Spin fluctuations effectively enhance the de-pairing Coulomb pseudopotential parameter $\mu_{\text{eff}}^* = \frac{\mu^* + \lambda_{\text{sf}}}{1 + \lambda_{\text{sf}}}$ and reduce the phonon-mediated attractive interaction $\lambda_{\text{eff}} = \frac{\lambda_{\text{ep}}}{1 + \lambda_{\text{sf}}}$, leading to a lower T_c [30], [35]. By postulating $\lambda_{\text{sf}} = 0.055$ for La_3Ni and stronger $\lambda_{\text{sf}} = 0.170$ for La_3Co we are able to consistently explain both the observed Sommerfeld parameter values and superconducting

critical temperatures, as shown in Table 4. This still requires the presence of a relatively strong electron-phonon interaction, especially in La_3Co , since the resulting value of the coupling parameter is $\lambda_{\text{ep}} = 1.42$.

The hypothesis of the presence of spin fluctuations is mainly based on the discrepancy of the computed Sommerfeld parameter compared to the measured one in La_3Co . To verify the theoretical result, additional computations were performed, using a different approach (full potential linearized augmented plane wave method, FP-LAPW, as implemented in the WIEN2k package [36]), with two different exchange-correlation potentials (Perdew-Wang [31] LDA and Perdew-Burke-Ernzerhof Generalized Gradient Approximation, PBE-GGA [37], as well as taking into account the spin-orbit coupling. All these computations yielded the total DOS at the Fermi level in a range $5.2 - 5.3 \text{ eV}^{-1}$ per f.u., consistent with the previous KKR result. The change of computational approach was not expected to have a large influence on $N(E_F)$ value, since E_F in La_3Co is placed in a local minimum of DOS. Also, since the sample quality is high, we do not expect any significant amount of impurities, which could either modify the band structure or affect the measured γ_{expt} value. Thus, spin fluctuations may be expected to exist in La_3Co compound, and may be responsible for the renormalization of the Sommerfeld parameter.

V. Summary and Conclusions

Physical properties of La_3Co and La_3Ni were examined through measurements of susceptibility, specific heat and resistivity. La_3Co is confirmed to be a bulk superconductor with $T_c \approx 4.6$ K. The value of the Ginzburg-Landau κ parameter indicates that La_3Co is a type-II superconductor. Results of resistivity versus temperature for La_3Co and La_3Ni show a metallic-like character ($d\rho/dT > 0$) and quadratic $\rho \sim T^2$ behavior at low temperature, which is stronger for the case of La_3Co . The theoretical calculations of the electronic structure show the characteristic features of the studied materials, with their Fermi levels placed in between the DOS peaks from transition-metal 3d and La 4f states. The comparison of the band structure of La_3Co with La_3Ni shows that La_3Ni exhibits a deep minimum in the DOS near E_F , which is not present in La_3Co , and could explain its lower T_c , reported in the literature (1.45 K), compared to 4.6 K observed in La_3Co [9]. The observed large difference of the computed Sommerfeld parameter γ_{calc} with the experimental value γ_{expt} suggests that in addition to the electron-phonon interaction, other mechanisms may be involved in renormalization of the electronic specific heat. Spin fluctuations are suggested as a possible second mechanism, and a moderate value of $\lambda_{\text{sf}} = 0.17$ allows one to explain both values of γ and T_c .

Acknowledgements

This project was financially supported by the National Science Centre (Poland) Grant No. DEC2012/07/E/ST3/00584. B.W was partially supported by the Polish Ministry of Science and Higher Education. Work at Los Alamos National Lab was performed under the auspices of the U.S. Department of Energy, Office of Science.

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