Structural investigation of Np$_2$Co$_{17}$ and analogue compounds under pressure

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The structural behavior of Np$_2$Co$_{17}$ is investigated by means of high-pressure diamond-anvil compression measurements and is compared with that of the isostuctural compounds Lu$_2$Co$_{17}$ and Lu$_2$Ni$_{17}$. The Th$_2$Ni$_{17}$-type hexagonal crystal structure is preserved with no measurable discontinuous volume collapses up to the highest achieved pressure, $p = 43$ GPa. For Np$_2$Co$_{17}$, fits to the Birch-Murnaghan and Vinet equations of state give values of the isothermal bulk modulus and its pressure derivative of $B_0 = 286$ GPa and $B_0'' = 3$, revealing that this Np compound is a highly incompressible solid with stiffness comparable to that of superhard covalently bonded materials. For the Lu$_2$T$_{17}$ (T = Co, Ni) compounds, the measured bulk modulus changes from $B_0 = 137$ GPa for $T =$ Co to $B_0 = 257$ GPa for $T =$ Ni. The isothermal equation of state for the studied compounds are in excellent agreement with the results of ab initio fully relativistic, full-potential local spin-density functional calculations. Theoretical estimates of the bulk modulus are given also for Np$_2$Ni$_{17}$, for which $B_0$ is predicted to assume values intermediate between those measured for Lu$_2$Ni$_{17}$ and Np$_2$Co$_{17}$.

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I. INTRODUCTION

Np$_2$Co$_{17}$ is a transuranic analog of the widely investigated Sm$_2$Co$_{17}$ high-performance permanent magnet [1,2]. It crystallizes in the P6$_3$/mmc ($D_{6h}$) space group with the Th$_2$Ni$_{17}$-type hexagonal structure. The unit cell is composed of 38 atoms with the Np atoms residing at 2$b$ and 2$d$ special positions, and the Co atoms at the 4$f$, 6$g$, 12$k$, and 12$j$ sites. The two Np sites have a similar Co nearest-neighbor environment but a different nearest Np coordination. However, crystallographic disorder, which is not uncommon for the rare earths analogues [3], may contribute to average the differences in the close surrounding of the two Np sites.

The magnetic properties of Np$_2$Co$_{17}$ have been recently investigated on the basis of magnetization, Mössbauer, and x-ray magnetic circular dichroism measurements [4]. Magnetization curves indicate the occurrence of ferromagnetic order below a $T_C > 350$ K. Mössbauer spectra suggest a Np$^{3+}$ oxidation state and give an ordered moment of $\mu_{Np} = 1.57(4) \mu_B$ and $\mu_{Co} = 1.63(4) \mu_B$ for the Np atoms located, respectively, at the 2$b$ and 2$d$ crystallographic positions. Combining these values with a sum rule analysis of the XMCD spectra measured at the neptunium $M_{4,5}$ absorption edges, the spin and orbital contributions to the site-averaged Np moment ($\mu_S = -1.88(9) \mu_B$, $\mu_L = 3.48(9) \mu_B$) have been determined. The ordered moment averaged over the four inequivalent Co sites, as obtained from the saturation value of the magnetization, is $\mu_{Co} \simeq 1.6 \mu_B$.

Lu$_2$T$_{17}$ (T = Co and Ni) also crystallize in the Th$_2$Ni$_{17}$-type hexagonal structure and are both ferromagnetic. The Co compound orders at $T_C = 1210$ K and exhibits a spontaneous magnetic moment at 5 K of 27.6 $\mu_B$ per formula unit (1.6 $\mu_B$ per Co atom). A spin reorienation from easy-plane to easy-axis type of magnetic anisotropy is observed at 740 K [5]. Lu$_2$Ni$_{17}$ has a $T_C$ of about 600 K and a Ni moment of 0.27 $\mu_B$, suggesting that almost all Lu valence electrons are transferred to the Ni 3$d$ band [6].

Here we report x-ray diffraction diamond-anvil cell (DAC) compression studies to 43 GPa for Np$_2$Co$_{17}$ and its isostuctural analogues Lu$_2$Co$_{17}$ and Lu$_2$Ni$_{17}$. We have measured the isothermal equation of state (EOS) and the ratio $c/a$ between the two lattice parameters defining the hexagonal unit cell. Using the third-order Birch-Murnaghan EOS [7–9] or the analytic approximation to the Vinet EOS [10] to fit the data, we have found that the bulk modulus $B_0$ increases from 137 GPa in Lu$_2$Co$_{17}$ to 286 GPa in Np$_2$Co$_{17}$. The latter value is among the highest reported for an intermetallic compound [11]. The bulk modulus we obtained for Lu$_2$Ni$_{17}$ is $B_0$ = 257 GPa, about 80% larger than for the Co analog and about 70% larger than for Er$_2$Fe$_{17}$ [12]. We have not been able to measure the compressibility of Np$_2$Ni$_{17}$, but ab initio calculations based on the local spin-density approximation (LSDA) do not predict a similar increase of $B_0$ if Ni is substituted for Co in Np$_2$Co$_{17}$.

The remainder of this paper is structured as follows. In Sec. II, we provide details on synthesis and experimental procedures; in Sec. III we present the experimental results and the fits to phenomenological EOS, whereas the results of first-principles electronic-structure calculations are presented in Sec. IV. A short summary and conclusions are found in Sec. V.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of Np$_2$Co$_{17}$ and Lu$_2$T$_{17}$ were prepared by arc melting stoichiometric amounts of high-purity elemental constituents (99.9% Np, 99.9% Lu, 99.999% Co and 99.999% T). 1098-0121/2014/90(5)/054107(6) 054107-1 Published by the American Physical Society
Ni) on a water-cooled copper hearth, under Ar (99.9999%) atmosphere. A Zr alloy was used as an oxygen getter. The weight losses during melting were less than 0.2%. The samples were melted five times to improve the homogeneity, then wrapped in tantalum foils, and annealed at 800 °C in evacuated quartz ampoules for 1 week. Phase analysis of the obtained ingots was performed before and after annealing. Crystallographic analyses were performed at room temperature by x-ray diffraction on samples with a mass of about 25 mg, ground, and dispersed on a Si wafer. Data were collected in back-reflection mode with a Bruker D8 diffractometer installed inside a α-γ glove box, using Cu-Kα1 radiation selected by a Ge (111) monochromator. A 1D position sensitive detector was used to cover the angular range from 15 to 120 degrees, with incremental steps of 0.0085 degrees.

About 10 μg of material were loaded into a membrane-type diamond anvil cell (DAC), affording a maximum x-ray scattering angle 2θmax ≈ 35°. Diamond culets were of 500-μm diameter with preindentled inconel gaskets of 200-μm (diameter) hole and (indented) thickness 30 μm. Pressure was calibrated by the ruby fluorescence method, using a single ruby-ball of diameter smaller than 10 μm. To avoid the risk of contamination of any exterior part of the DAC, the Np2Co17 powders were combined with a small amount of epoxy resin to form solid (“granular”) pieces, which were loaded into the DAC. Sample loading of the DAC was done in inert atmosphere inside a glove box to protect the sample from moisture and air, as well as to provide confinement for the radioactive material. Safety regulations impose sealing the DAC by application of a finite pressure pmin before removal to the x-ray diffractometer. For this reason, diffraction patterns for pressures smaller than pmin cannot be recorded. In this study, pmin = 4.3 GPa. Attention must also be paid to the pressure-transmitting medium being used, to assure that it will not cause sample degradation (alcohol, for instance, in presence of a high radiation field in a confined space can be decomposed to aggressive products), or risks of radioactive contamination upon decompression (for instance in the case of liquefied gases such as Ar or N2). A common choice in high-pressure studies of transuranium materials is to use silicone oil, although it is known that a quasihydrostatic behavior with this medium is achieved only in a restricted pressure range [13]. This fact has been taken into account in the data analysis, as reported below.

Measurements were performed at ITU, Karlsruhe, from 4.3 up to 43 GPa using a modified Bruker D8 x-ray diffractometer with focusing mirror optics installed on a Bruker molybdenum rotating anode x-ray source. X-ray wavelength and spot-size at the sample position were 0.70926 Å (Mo Kα1) and 100 × 100 μm². Diffraction images were recorded with a Bruker SMART Apex II charge-coupled device (CCD), 1024 × 1024 pixels of dimensions 61 × 61 μm². The DAC was rotated through a sample angle ∆θ ≈ ±4° while collecting each diffraction image. The DAC to sample distance and CCD nonorthogonality corrections were calibrated using powder diffraction from a LaB6 standard. The images were integrated using the ESRF FIT2D software [14], which generates files suitable for profile refinement. Rietveld and Le Bail refinement techniques have been used to determine the variation of the lattice parameters with increasing pressure.

Vickers microhardness measurements have been performed with a Leitz miniload 2 durometer put inside a α-γ glove box. For these measurements we also prepared samples of the isostructural compounds Np2Ni17. Indentation was performed by applying a load of 200 N to polished samples having a flat surface of about 20 mm². Hardness values have been obtained by averaging the results of nine independent measurements for each sample.

### III. EXPERIMENTAL RESULTS

The ambient-pressure powder diffraction pattern of Np2Co17 is shown as an example in Fig. 1. The Rietveld analysis was performed with the X’Pert HighScore Plus software package of PANalytical. The background was fitted with a polynomial, and the shape of the Bragg peaks was described by a pseudo-Voigt function. The observed Bragg peaks for all three investigated compounds can be indexed in the hexagonal P63/mmc space group, with lattice parameters given in Table I. The best fit was obtained assuming full occupation of the sites corresponding to the ideal Th2Ni17-type structure. The structural parameters are also reported in Table I. The crystal structure, shown in the inset of Fig. 1, consists of three different planes stacked perpendicularly to the c axis in the sequence ABAC. Planes A contain Co (Ni) atoms located at 6g and 12k positions, planes B and C contain both 12j Co (Ni) atoms and Np (Lu) at 2b and 2d sites. The transition metal atoms at 4f positions form a dumbbell arrangement separating A, B, and C planes.

Examples of angle-dispersive x-ray diffraction results for Np2Co17 at different applied pressures are shown in Fig. 2, whereas an example of profile-fitted diffraction data is shown in Fig. 3. Peak broadening did not affect the quality of the refinements up to 30 GPa. For higher pressure, some principal
TABLE I. Refined structural parameters for Np<sub>2</sub>Co<sub>17</sub> and Lu<sub>2</sub>Ni<sub>17</sub>, at room temperature and ambient pressure. The parameters are referred to the hexagonal axes (space group P<sub>6</sub><sup>3</sup>/mmc). Full occupation were assumed for all sites. Np(Lu) atoms reside at 2<sup>b</sup>(¯6</sup>m</sup>2</sup>,001</sup>/4) and 2<sup>d</sup>(¯6</sup>m</sup>2</sup>,1/32</sup>/3</sup>3/4) sites; Co<sub>2</sub>(Ni<sub>2</sub>) reside at the 6<sup>g</sup>(2/m,1/200) site. The lattice parameters obtained at room temperature for Lu<sub>2</sub>Co<sub>17</sub> are <i>a</i> = 8.2529(2) Å and <i>c</i> = 8.1060(5) Å.

<table>
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<tr>
<th>Atom</th>
<th>Site</th>
<th>Site</th>
<th>&lt;i&gt;x&lt;/i&gt;</th>
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<td>Co&lt;sub&gt;1&lt;/sub&gt;</td>
<td>4&lt;sup&gt;f&lt;/sup&gt;</td>
<td>1/3</td>
<td>2/3</td>
<td>0.1048(5)</td>
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<tr>
<td>Co&lt;sub&gt;3&lt;/sub&gt;</td>
<td>12&lt;sup&gt;j&lt;/sup&gt;</td>
<td>0.3241(5)</td>
<td>0.9547(3)</td>
<td>1/4</td>
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<tr>
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<td>12&lt;sup&gt;k&lt;/sup&gt;</td>
<td>0.1663(3)</td>
<td>0.3326(6)</td>
<td>0.9775(3)</td>
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<td>Lu&lt;sub&gt;2&lt;/sub&gt;Ni&lt;sub&gt;17&lt;/sub&gt;</td>
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<td>Ni&lt;sub&gt;1&lt;/sub&gt;</td>
<td>4&lt;sup&gt;f&lt;/sup&gt;</td>
<td>1/3</td>
<td>2/3</td>
<td>0.1094(3)</td>
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<tr>
<td>Ni&lt;sub&gt;3&lt;/sub&gt;</td>
<td>12&lt;sup&gt;j&lt;/sup&gt;</td>
<td>0.3279(3)</td>
<td>0.9594(2)</td>
<td>1/4</td>
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<tr>
<td>Ni&lt;sub&gt;4&lt;/sub&gt;</td>
<td>12&lt;sup&gt;k&lt;/sup&gt;</td>
<td>0.1657(1)</td>
<td>0.3315(3)</td>
<td>0.9810(2)</td>
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Reflections become masked by gasket peaks and the spectrum quality deteriorates. The hexagonal ambient-pressure crystallographic structure is preserved over the investigated pressure range, the lattice being compressed continuously.

The experimental isotherm EOS for the three compounds is shown in Fig. 4. The results have been fitted with a third-order Birch-Murnaghan EOS [7–9],

\[
p(V) = \frac{3}{2} B_0 \left[ \left( \frac{V}{V_0} \right)^{-\frac{7}{3}} - \left( \frac{V}{V_0} \right)^{-\frac{1}{3}} \right] \times \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[ \left( \frac{V}{V_0} \right)^{-\frac{1}{3}} - 1 \right] \right\},
\]

where <i>p</i> is the applied pressure, <i>V</i> is the ambient-pressure unit cell volume, <i>B_0</i> is the isothermal bulk modulus, and <i>B'_0</i> its pressure derivative. The resulting fits are shown by solid lines in Fig. 4 and give <i>B_0</i> = (286 ± 5) GPa and <i>B'_0</i> = 3 for Np<sub>2</sub>Co<sub>17</sub>, <i>B_0</i> = (137 ± 1) GPa and <i>B'_0</i> = 5 for Lu<sub>2</sub>Co<sub>17</sub>, and <i>B_0</i> = (257 ± 2) GPa and <i>B'_0</i> = 2.5 for Lu<sub>2</sub>Ni<sub>17</sub>. As mentioned before, silicone oil has a quasihydrostatic behavior only in a restricted pressure range. For this reason, the fits have been performed using data in different pressure intervals, first up to 14 GPa and then up to 32 GPa. The difference between the values for the fitted parameters in the two cases determines the quoted experimental uncertainties. In the case of the Lu compounds, two independent diffraction data sets have been collected, obtaining the same results within experimental errors.

As an alternative approach to determine the bulk modulus for the three samples, the analytic approximation to the Vinet equation
The adopted set of valence basis states was 5 local orbital method (RFPLO) [16]. In this scheme the exchange-correlation (XC) potential in LSDA was used [17]. EOS [10] was also used:

\[ p(V) = 3B_0 \left(1 - \frac{f_V}{f}\right) \exp \left[ \frac{3}{2}(B_0' - 1)(1 - f_V) \right]. \]

where \( f_V = (V / V_0)^{1/3} \). The results of the two approaches are fully consistent (see Table II).

### IV. AB INITIO CALCULATIONS AND COMPARISON WITH EXPERIMENTAL RESULTS

*Ab initio* density-functional theory calculations were performed with the relativistic version [15] of the full potential local orbital method (RFPLO) [16]. In this scheme the four-component Kohn-Sham-Dirac equation, which implicitly contains spin-orbit coupling up to all orders, is solved self-consistently. The Perdew-Wang parametrization of the exchange-correlation (XC) potential in LSDA was used [17]. The adopted set of valence basis states was 5f; 6s6p6d; 7s7p for Np, 4f; 5s5p5d; 6s6p for Lu, and 3d; 4s4p for Co and Ni. The ground state properties have been calculated assuming a nonmagnetic configuration. The self-consistent determination of the Np 5f occupancy number led to a value of 3.8, supporting the assumption that Np ions in Np2T17 are practically trivalent.

Total energy calculations were performed as a function of volume, for a \( 10 \times 10 \times 10 \) k mesh, corresponding to 84 k vectors in the irreducible wedge of the tetragonal Brillouin zone. The unit cell contains 38 atoms. The volume dependence of the cohesive energy \( E(V) \) is then obtained from the total energies by subtracting isolated atom contributions. The equation of state at 0 K is finally calculated from the variation of the cohesive energy with respect to volume, \( P = -\partial E / \partial V \), and is compared to experimental values in Fig. 5. We note that the experimental compressibility curves have been obtained at room temperature. The experimental volume differs, therefore, from the zero-temperature volume by the effect of the thermal expansion, which is neglected. This is a good approximation, because we consider the relative volume, \( V(p) / V_0 \), in which the thermal expansion is practically canceled. Experimental and theoretical values for the bulk modulus and its first pressure derivative are compared in Table III.

### V. DISCUSSION AND CONCLUSIONS

The results reported above reveal that Lu2Ni17 has a bulk modulus only twice as large as the isoelectronic compound Lu2Co17 and falls under the less compressible intermetallics [11,18]. The large variation observed between the two compounds is surprising, for empirical models would rather predict a similar value for their bulk modulus \( B_0 \) [11,18]. The most striking difference between the two compounds concerns their magnetic properties. Both are ferromagnetic, but the Co atoms in Lu2Co17 carry on average a magnetic moment that is about a factor six larger than the average Ni magnetic moment in Lu2Ni17. This suggests that the Ni 3d band is almost filled, so that the valence electron density at the transition metal site is larger in the nickel compound. A larger valence electron density usually leads to a higher bulk modulus. Np2Co17 has also a \( B_0 \) more than twice as large as Lu2Co17, with a value approaching that of stishovite (291 GPa, Ref. [19]) and cubic BN (369 GPa, Ref. [20]). However, the Co sublattice in the Np and Lu analogs has essentially the same magnetization. In this case, the difference in \( B_0 \) could be due to the participation to bonding of the partially localized Np 5f electrons [4].

First-principles simulations for Np2Ni17 do not predict an increase of \( B_0 \) as the one observed for Lu2T17 upon substitution of Co for Ni. For technical reasons, we have not been able to perform x-ray diffraction compressibility studies for Np2Ni17. However, the agreement between theoretical predictions and experimental values for the other compounds investigated here lends credibility to the calculations, which exclude an extremely high value of \( B_0 \) for Np2Ni17. Whereas the other three compounds examined in this study are ferromagnetic above room temperature, Np2Ni17 remains paramagnetic down to 17 K, where a transition to a complex antiferromagnetic phase occurs [21]. This suggests that the electronic structure of the A2T17 compounds (A = Np, Lu) is very sensitive to lattice substitution. It is plausible that the Np 5f electrons in Np2Ni17 are even more localized than in Np2Co17 and do not participate substantially to bonding. This could naively explain the similar values of \( B_0 \) found for the two A2Ni17.

So far, the material with the highest known bulk modulus is osmium [22] (\( B_0 = 462 \) GPa), followed by diamond [23] (\( B_0 = 443 \) GPa), which is also the hardest known material. Indeed, in many instances, a high bulk modulus is correlated with a high mechanical hardness [24], although the first property determines the response to elastic deformations, the second one is related to the capacity of the material to resist plastic deformation. For the compounds investigated here, hardness measurements show that they are only moderately hard, with a Vickers hardness number in the range \( 6-7 \) GPa. Table III gives the results obtained by a Vickers microhardness tester and shows that the variations of hardness
are not correlated with compressibility, probably because of the presence of lattice defects in the indented samples.

In conclusion, the results of diamond-anvil cell x-ray diffraction compression studies of Np$_2$Co$_{17}$ show that this compound is characterized by a very large bulk modulus, whose value approaches those of the least compressible known materials. The $B_0$ value measured for Np$_2$Co$_{17}$ is about twice as large as the one measured for the isostructural compound Lu$_2$Co$_{17}$ but comparable to the value measured for Lu$_2$Ni$_{17}$. First-principles electronic structure calculations reproduce well the equation of state experimentally determined for Np$_2$Co$_{17}$ and Lu$_2$Ni$_{17}$. These calculations predict for Np$_2$Ni$_{17}$ a value of $B_0$ close to the one obtained for the Lu analog. The four compounds are moderately hard and, despite the large differences in their bulk modulus, have polycrystalline Vickers microhardness of comparable value.

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