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Role of carbon in $AlCNi_3$ and $GaCNi_3$: A density functional theory study

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In this paper we report first-principles calculations on the ternary antiperovskites $AlCNi_3$ and $GaCNi_3$. We find that in contrast to recent experimental results $AlCNi_3$ and $GaCNi_3$ are nonmagnetic metals. Taking into account data from the literature as well as our own calculations, we have evidence that some of the recent experiments on $AlCNi_3$ and $GaCNi_3$ may have been performed on samples with carbon deficiencies. We believe that the conclusions which have been drawn from these experiments caused several misinterpretations. First, neither in our density functional theory (DFT) calculations for $AlCNi_3$ nor in those for $GaCNi_3$ do we find indications for a magnetic ground state ($AlCNi_3$) or the presence of strong electron-electron correlations ($GaCNi_3$). Second, we find that the local density approximation (LDA) and in particular the generalized gradient approximation (GGA) are well suited for a proper description of these compounds. The unusually large volume differences between the LDA calculations and some experiments are thus rather due to a comparison with substoichiometric samples. By employing accurate full-potential DFT calculations using both the LDA and the GGA we performed fixed spin moment calculations in order to estimate the Stoner enhancement factors S. In addition we investigated $TC_{0.5}Ni_3$ with $T=$Al and Ga and found that the density of states at the Fermi energy is expected to increase about linearly upon lowering the carbon concentration. This explains the tendencies toward magnetism found in experiment, since for the carbon-free border compounds $AlNi_3$ and $GaNi_3$ their proximity to ferromagnetic order is well established.

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I. INTRODUCTION

Since the discovery of superconductivity in $MgCNi_3$[1] there has been great interest in related, isostructural so-called cubic antiperovskites of the type $TCNi_3$, where T denotes either divalent (Zn) or trivalent (Al, Mg) elements. $ZnCNi_3$ has already been investigated intensively,[2,3] mainly due to its close similarity to the superconductor $MgCNi_3$. However, the situation is different for $AlCNi_3$ and $GaCNi_3$. Even though experimental results have been published, to our knowledge no theoretical investigation of the magnetic properties of $AlCNi_3$ and in particular no theoretical investigation of $GaCNi_3$ has been done. For $GaCNi_3$ Tong *et al.*[4] performed specific heat measurements indicating the presence of strong electron-electron correlations, whereas for $AlCNi_3$, Dong *et al.*[5] did magnetization measurements revealing weak ferromagnetism. Our motivation is not only to investigate the ground states of these compounds; we also want to clarify several unresolved issues found in the literature. The lattice constant of $AlCNi_3$ determined by Dong *et al.*[5] is significantly smaller (by 5.6%) than the value reported earlier by Goodenough *et al.*,[6] who did systematic studies on this class of compounds. For $GaCNi_3$ Tong *et al.*[4] recently published a lattice constant of 3.6 Å, which curiously is almost identical to the older value of L'Heritier *et al.* for a sample with nominal composition $GaC_{0.1}Ni_3$.[7] Thus there seems to be a disagreement between old data and some of the new experiments. In density functional theory (DFT) calculations Okoye *et al.*[8] reported a rather huge disagreement between their calculated [local density approximation (LDA)] lattice constant and the experimental one for $AlCNi_3$.[5] The LDA seems to overestimate the cell volume, which is very unusual. For $ZnCNi_3$ a similar but less pronounced disagreement regarding lattice constants exists. In this context Johannes *et al.*[2] argued that carbon deficiencies could be the reason.

Employing the full-potential linearized augmented plane-wave method[9] we perform fixed spin moment calculations for $TCNi_3$ with $T=$Al, Ga, Mg, and Zn in order to probe these systems' responses to an external magnetic field. We find that $GaCNi_3$ and $AlCNi_3$ are nonmagnetic metals with a low Stoner enhancement factor S and thus far away from a magnetic ground state. This behavior is found within both the LDA and the generalized gradient approximation (GGA). It is important to mention that a comparative analysis between the LDA and GGA is crucial for a metallic system at the border of a magnetic instability (for more details see our recent paper[10]). In addition we investigate carbon-deficient samples and will show that the lack of carbon leads to an enhancement of the tendency toward magnetism. This is not surprising if one bears in mind that isostructural $AlNi_3$ and $GaNi_3$, which can be obtained from the ternary antiperovskites by the complete removal of carbon, are close to a ferromagnetic quantum critical point. In order to show the similarities and differences between the compounds with and without carbon from the viewpoint of powder x-ray diffraction, we finally discuss theoretical x-ray spectra. With this additional information we have another hint at hand indicating that the tendency toward magnetism found in recent experiments for $GaCNi_3$ and $AlCNi_3$ is an artifact stemming from carbon-deficient samples, and that truly stoichiometric ones are not at the border of magnetism. The interesting physical properties of the carbon-free compounds $AlNi_3$ and $GaNi_3$, including strong magnetic fluctuations due to the proximity to a ferromagnetic quantum critical point (QCP), make $TCNi_3$ also highly interesting materials. One could, for example, tune them very slowly toward this QCP by changing the carbon concentration.

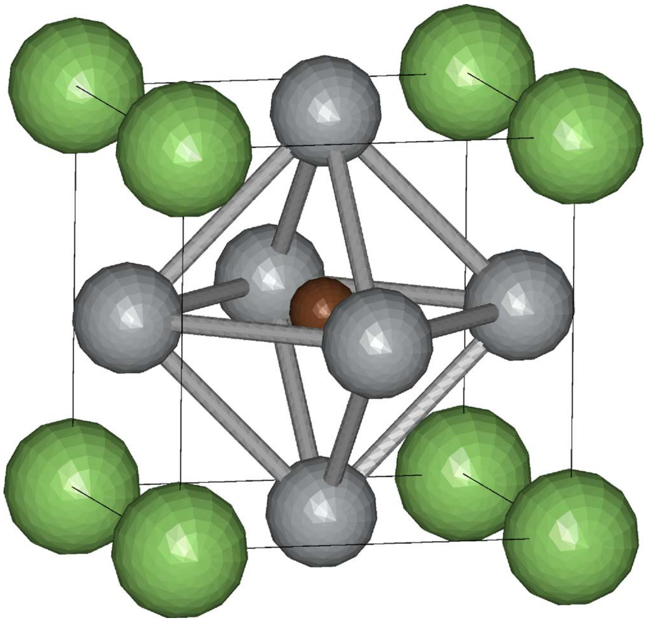

FIG. 1. (Color online) Unit cell of the cubic antiperovskites TCNi$_3$. T is situated in the corner, carbon in the center, and Ni occupies the face centers as in fcc Ni.

II. COMPUTATIONAL METHOD

The calculations were performed using the FLAIR code,[11] an implementation of the full-potential linearized augmented plane-wave method.[9] Exchange and correlation were treated within the local density functional formalism[12] using either the parametrization of Perdew and Zunger[13] and Ceperley and Alder[14] (LDA) or that of Perdew, Burke, and Ernzerhof[15] (GGA). The potential and charge density were expanded up to $l=8$ and $G_{\mathrm{max}}=12$ a.u.$^{-1}$ Inside the muffin tin spheres ($r=2.5$ bohr for Ga or Al, $r=1.4$ bohr for carbon, and $r=2.05$ bohr for Ni) the wave functions were expanded up to $l=8$ and a plane-wave cutoff k_{max} of $7/\min(r_{MT})$ was used, where $\min(r_{MT})$ denotes the radius of the smallest muffin-tin sphere in the cell (carbon). A **k**-mesh sampling with at least 120 **k** points in the irreducible wedge of the Brillouin zone for lattice optimizations and at least 220 irreducible **k** points for fixed spin moment calculations was used.

III. RESULTS AND DISCUSSION

A. AlCNi$_3$ and GaCNi$_3$

The antiperovskite unit cell of TCNi$_3$ with T=Mg, Zn, Al, and Ga contains one formula unit and is shown in Fig. 1. The T element is situated in the corner of the cube, C in the center, and Ni occupies the face centers. All compounds are metals, and the Ni d shell is partially filled also if the T cation is formally trivalent. The density of states (DOS) is plotted in Fig. 2. Carbon p and T p states have been multiplied by a factor of 10 and are shown in part (b) of each plot. In both materials, E_F is situated in a region with predominantly Ni d states [mainly (d_{xz},d_{yz}) and $d_{x^2-y^2}$], followed by C p and small contributions of T p states. The peak below E_F, which is responsible for the tendency toward magnetism in ZnCNi$_3$ and especially MgCNi$_3$,[18–20] has mainly (d_{xz},d_{yz}) character. In GaCNi$_3$, the carbon states are situated slightly higher in energy than in the Al compound, and the reduced lattice constant causes the d states to be slightly narrower ($\approx$70 meV). While in AlCNi$_3$ E_F is situated within a local minimum in the LDA and GGA, in GaCNi$_3$ E_F is situated in a local maximim and a local minimum within the LDA and GGA, respectively. Nevertheless, the absolute values in all cases are much below the value necessary for magnetic instabilities.

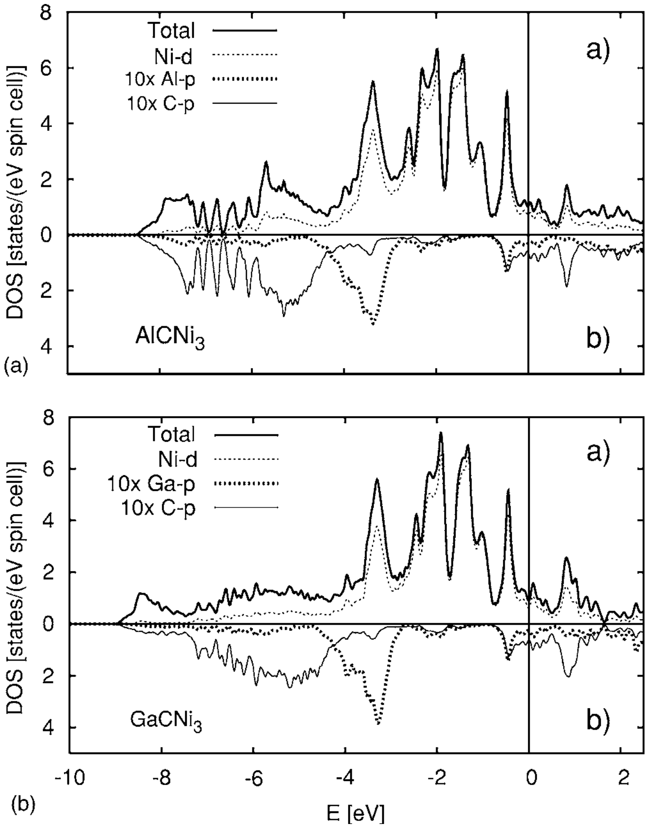

FIG. 2. Density of states (DOS) for AlCNi$_3$ (top) and GaCNi$_3$ (bottom). In (a), GGA results for the total and Ni d resolved DOS are shown. In (b) the Al or Ga p and C p states multiplied by 10 are plotted.

A list of lattice constants for the series TCNi$_3$, obtained via a fit to the Murnaghan equation,[21] is given in Table I. With a_{DFT} we denote theoretical results and with a_{expt} measured ones. AlNi$_3$ and GaNi$_3$ are given on the right-hand side of the table. While for MgCNi$_3$ calculated and measured lattice constants are in good agreement (in particular for the GGA), already in the case of ZnCNi$_3$ deviations occur. This has already been addressed by Johannes *et al.*,[2] who argued that carbon deficiencies might be responsible. Regarding AlCNi$_3$, the biggest discrepancy among experimental values has been found. A comparison with AlNi$_3$ shows that the additional carbon in the perovskites unambiguously leads to an increase in the cell volume. Thus it is plausible to compare calculated results with those of Goodenough *et al.*,[6] whose lattice constant for AlCNi$_3$ is the bigger one of the two values listed. This value (3.80 Å), however, is in good agreement with our GGA result, only the LDA underesti-

TABLE I. Calculated (a_{DFT}) and measured (a_{expt}) lattice constants of the cubic antiperovskites TCNi$_3$ with T=Mg, Zn, Al, and Ga as well as of $AlNi_3$ and $GaNi_3$, which can be obtained from the former by removing carbon. In parentheses theoretical results obtained by other groups are listed.

		$MgCNi_3$	$ZnCNi_3$	$AlCNi_3$	$GaCNi_3$	$AlNi_3$	$GaNi_3$
a_{expt} (Å)		3.81[a]	3.66,[b] 3.77[c]	3.587,[d] 3.80[c]	3.604[e]	3.568[f]	3.576[f]
a_{DFT} (Å)	LDA	3.74	3.69 (3.679)[g]	3.70 (3.697)[h]	3.71	3.47	3.49
	GGA	3.82	3.78	3.78 (3.774)[h]	3.79	3.56 (3.574)[i]	3.58 (3.591)[i]

[a] Reference 1.
[b] Reference 3.
[c] Reference 6.
[d] Reference 5.
[e] Reference 4.
[f] Reference 16.
[g] Reference 2.
[h] Reference 8.
[i] Reference 17.

mates the lattice constant more strongly than one would expect. When $GaCNi_3$ is considered, there is—to our knowledge—only one experimental value available (3.6 Å), which is almost identical to that of L'Heritier *et al.*,[7] who give a stoichiometry $GaC_{0.1}Ni_3$. Thus we expect the truly stoichiometric compound GaC_1Ni_3 to have a lattice constant of approximately 3.78(4) $Å$, close to our GGA result. For the border compounds $AlNi_3$ and $GaNi_3$, listed in the right-hand side of the table, again our GGA calculations yield a cell volume almost identical to the experimental one, whereas LDA calculations as usual underestimate the experimental lattice constants by 2.7% and 2.4% for $AlNi_3$ and $GaNi_3$, respectively. These findings clearly show that the GGA is much better suited for a proper description of these compounds.

In our DFT-based calculations $AlCNi_3$ and $GaCNi_3$ are clearly nonmagnetic at their equilibrium lattice constants in both the LDA and GGA. In order to assess whether these compounds are close to magnetism or not we performed fixed spin moment calculations, which allow for an estimation of the Stoner enhancement factors S. First we tried to fit the total energy E (in eV) vs the total magnetization per unit cell, M (in μ_B) via a quadratic function of the form $E=E_0+aM^2$. This method yields rather unsatisfactory results. For the divalent compounds, T=Zn and Mg, the prefactor a depends sensitively on the fit interval. For small magnetic moments a is much smaller and the system much closer to magnetism than for large moments. This problem is also present in the compounds with trivalent Al and Ga, even though much weaker. In literature the deviation of $E(M)$ from a quadratic behavior is a well-known problem [e.g., in $MgCNi_3$ (Ref. 18)] and it can be circumvented by applying extended Stoner theory,[22] in which $\tilde{N}(m)$, an average between the DOS at E_f for spin-up and spin-down electrons is used. However, we used a different and very successful technique, which exploits the spin splitting Δ between spin-up and spin-down states on Ni and the relation $\Delta=M_{loc}I$. M_{loc} (in μ_B) denotes the local magnetic moment inside one Ni muffin tin sphere (r=2.05 a.u.), Δ is the spin splitting given in eV, and I is the so-called Stoner I. In this method the DOS at E_F and I are related to one Ni atom. As required for a proper analysis, I turned out to be rather insensitive to the chemical environment, not only among all the ternary compounds but also in comparison to elemental Ni ($I_{\mathrm{Ni}}=1.18$). For all compounds the Ni d peak situated approximately 0.5 eV below E_F has been used as a reference state for the determination of Δ. In order to get accurate results we averaged $I=\Delta/M_{loc}$ over ten different values of M_{loc} (for each compound), and M_{loc} was tuned by fixing several values of the total magnetic moment per cell. Finally S was determined via the relation $S=1/[1-N^{1\times\text{Ni-}d}(E_f)I]$, $N^{1\times\text{Ni-}d}(E_f)$ denoting the d-like DOS at E_f attributed to one Ni atom and one spin channel. The results of this analysis are listed in Table II. One can easily see that in the compounds with trivalent Al

TABLE II. Total DOS [$N^{tot}(E_F)$] as well as total Ni d DOS [$N^{\mathrm{Ni}\ d}(E_F)$] (for three Ni) at E_F for one spin direction calculated for the ternary anti perovskites. Listed are further I and S determined via the spin splitting. In the bottom the calculated molar Pauli paramagnetic susceptibility χ (10^{-4} emu/mol) and the calculated γ coefficient of the electronic contribution to the specific heat mJ/(mol f.u. K^2) are given.

		$MgCNi_3$		$ZnCNi_3$		$AlCNi_3$		$GaCNi_3$	
Quantity	Unit	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA
$N^{\mathrm{tot}}(E_F)$	[states/(eV f.u. spin)]	2.67	2.07	2.18	2.29	0.84	1.04	1.18	0.91
$N^{\mathrm{Ni}\ d}(E_F)$	[states/(eV Ni d spin)]	1.97	1.52	1.64	1.72	0.58	0.73	0.82	0.63
I	(eV)	0.99	1.16	1.01	1.17	1.03	1.15	1.01	1.11
S		2.9	2.4	2.2	4.3	1.2	1.4	1.4	1.3
χ^{mol}	(10^{-4} emu/mol)	1.73	1.34	1.41	1.48	0.54	0.67	0.76	0.59
γ	[mJ/(mol f.u. K^2)]	12.6	9.8	10.3	10.8	4.0	4.9	5.6	4.3

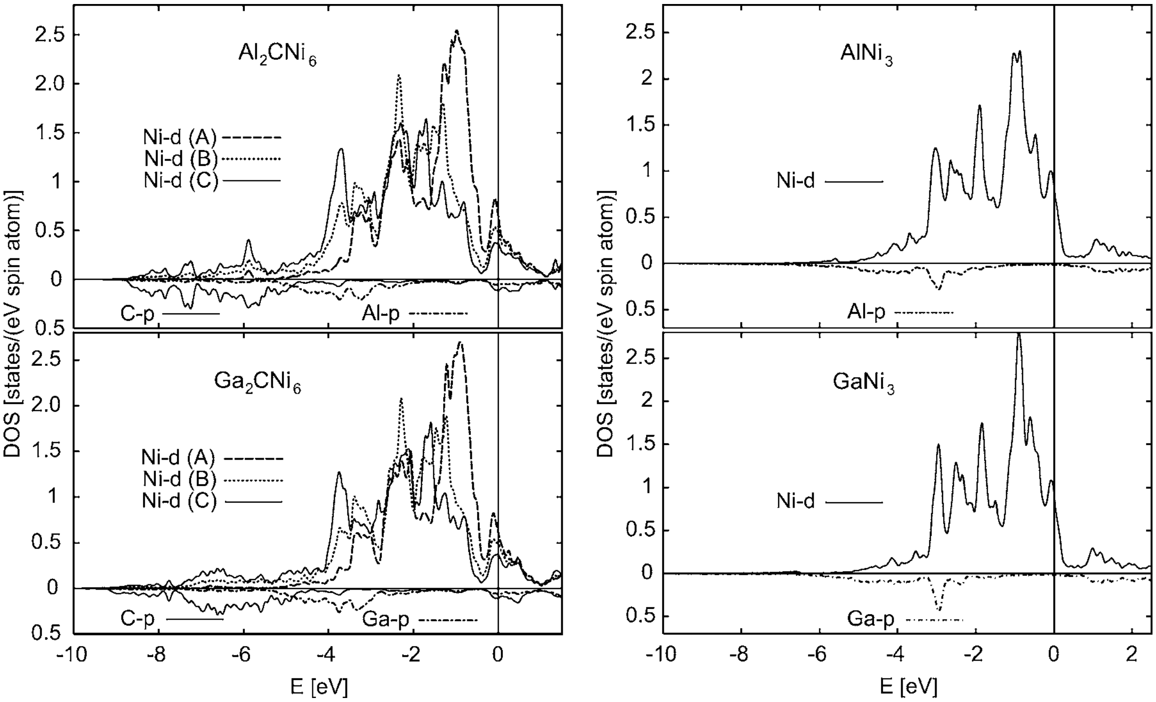

FIG. 3. Left panel: Total as well as projected DOS for Al_2CNi_6 (top) and Ga_2CNi_6 (bottom). Ni d sites with no (A), one (B), and two (C) nearest neighbor carbon sites are split; p states are plotted in the $y<0$ regime. Right panels: DOS of the compounds $AlNi_3$ and $GaNi_3$; Al and Ga p states are plotted in the $y<0$ regime.

and Ga the Stoner enhancement factor S is even slightly smaller than for T=Mg and Zn, which are known to be nonmagnetic. The strong differences between Mg and Zn and between the LDA and GGA are due to the proximity of the sharp Ni peak to E_f. The DOS at E_F is very sensitive to computational approximations (exchange correlation potential, potential and charge density expansion, and so on) and hence the results of different groups scatter strongly. Moreover, the error in S is huge when the product NI approaches 1. The compounds with T=Al and Ga, however, do not exhibit this sensitivity since they are much further away from a magnetic instability. They all have S values below 1.5. In order to allow for an easier comparison with experiment, we also listed the Sommerfeld constant γ^{th} and the Pauli paramagnetic susceptibility χ_p^{th} for the noninteracting electron gas, given by $\gamma^{th}=\pi^2/3k_B^2N(E_f)$ and $\chi_p^{th}=\mu_B^2N(E_F)$, $N(E_F)$ denoting the total DOS at E_f for both spin channels. In experiment Tong *et al.* determined for $GaCNi_3$ a γ value of 30 mJ/(mol K^2) and a χ_p^{th} around 3.9×10^{-3} emu/mol. They estimated $N(E_F)$ to be around 1.6 states/(eV spin unit) resulting in a Stoner enhancement S around 30. This is in disagreement with our calculations showing no signs of magnetic fluctuations. When $AlCNi_3$ is concerned, our $N(E_F)$ is in agreement with calculations made by Okoye *et al.*, but weak ferromagnetism as suggested by Dong *et al.* seems to be unlikely, provided that stoichiometric samples are considered.

In conclusion, in the compounds with trivalent elements (Al and Ga) the Fermi energy is well separated from the uppermost Ni d peak and consequently the DOS at E_f is situated between 0.8 to 1.2 states/(eV cell spin). Since the Stoner I is almost constant (as it should be) also the Stoner enhancement factors S, independently of whether the LDA or the much more appropriate GGA approximation is used, are below 1.5.

B. The role of carbon in $TCNi_3$

In order to figure out the role of carbon for magnetism we compared the results above with those obtained for T_2CNi_6 (doubled unit cell) and the carbon-free compounds TNi_3. It is well known that $GaNi_3$ is an enhanced Pauli paramagnet, whereas $AlNi_3$ is a weak ferromagnet.[23,24] Both are ferromagnetic in our calculations, but this is a well-known problem. The failure of the LDA particularly for $GaNi_3$ is due to the unsatisfactory description of spin fluctuations, which are associated with the ferromagnetic quantum critical point.[24] These fluctuations are stronger in the Ga compound, and even though (from experiment) $AlNi_3$ is closer to magnetism (actually it is magnetic) than $GaNi_3$, calculations result in the opposite. For the further discussion we will neglect these difficulties since it is only important to realize that in the present case the LDA and in particular the GGA at their equilibrium lattice constants overestimate but never underestimate the tendency toward magnetism. In Fig. 3 one can see easily the increase of the DOS at E_f when carbon is removed. The lack of one carbon atom in T_2CNi_6 splits the six Ni atoms into three groups of two members each. Ni of the first type (labeled as A) has no nearest neighbor carbon, Ni of the second type (B) has one nearest neighbor carbon and the third type of Ni (C) has two carbon atoms as nearest neighbors. The DOS for types, A, B, and C is plotted separately in Fig. 3. The lower the number of carbon atoms in the neighborhood of Ni becomes, the higher is the DOS at E_f. This is due to the reduced Ni-C hybridization and the resulting narrowing of the Ni d bands. We further examined the total DOS at E_f for GaC_xNi_3 with $x=1$, 0.5, and 0 (GGA results only) by setting up tetragonal supercells with doubled dimension in the z direction. We found that $N(E_F)$ varies about linearly with the carbon concentration, increasing by about 1.10(2) states/($AlNi_3$ spin) upon a reduction of x by 0.5. On the basis of these considerations we believe that within the series GaC_xNi_3 no magnetism will be found; only strong spin fluctuations are expected close to $x\approx 0$. For AlC_xNi_3 $N(E_F)$ also increases linearly by about 0.89(3) states/($AlNi_3$ spin) when 50% of C atoms are removed. However, since $AlNi_3$ is a weak ferromagnet, also AlC_xNi_3 with x sufficiently close to 0 will be magnetic. In the supercell calculations described above we neglected relaxations and assumed a linear variation of the lattice constants upon a variation of the carbon concentration. As a reference we used our GGA-based values for $AlNi_3$ and $GaNi_3$ (3.56 and 3.58 Å) as well as $AlCNi_3$ and $GaCNi_3$ (3.78 and 3.79 Å). These approximations are reasonable and allow us to roughly estimate the carbon concentration of the samples measured in experiment,[4,5] provided that these samples indeed were homogeneous and substoichiometric with respect to carbon. In the case of $GaCNi_3$, Tong *et al.*[4] find a lattice constant of 3.587 Å, which would result in a C concentration of 11%, if based on our GGA results and the above approximations. However, for a carbon concentration as low as ≈11% strong spin fluctuations are plausible due to the proximity to the quantum critical border compound $GaNi_3$. For $AlCNi_3$ the same analysis results in an estimation of 14% of carbon in the sample measured in Ref. 5, which gives a possible explanation for the weakly itinerant magnetic order the authors found.

C. Powder x-ray diffraction

From the viewpoint of powder x-ray diffraction experiments, Cu_3Au-type TNi_3 and antiperovskite type $TCNi_3$ are closely related. Both belong to the same space group ($Pm\bar{3}m$) and consequently have the same selection rules for Bragg peaks. Thus we calculated theoretical powder x-ray spectra of $TCNi_3$ and TNi_3 for $T=$Mg and Al by using the program POWDERCELL.[25] In all simulations we fixed the lattice constant to a value of 3.62 Å. While the differences between the Al and Mg compounds are negligible, the presence of carbon is clearly visible and can best be observed by comparing the intensity of the (1 0 0) and the (1 1 0) peaks. Assuming coherent x-ray scattering, the intensity of a certain peak is proportional to the absolute square of the structure factor, which itself is a sum over atomic form factors (assumed to be specific for one atomic species) multiplied with a phase factor. The crucial point is the phase factor of carbon, which changes sign from −1 to +1 when changing from the (1 0 0) to the (1 1 0) peak. Thus the additional presence of carbon will lead to a higher intensity of the (1 0 0) and a reduced intensity of the (1 1 0) peak. For the further discussion we define R as the ratio between these intensities, namely, $R=I_{(1\ 0\ 0)}/I_{(1\ 1\ 0)}$. While R is approximately 1.2 and 1.3 for the carbon-free compounds $AlNi_3$ and (hypothetical) $MgNi_3$, respectively, it increases to 3.6 for $AlCNi_3$ and 4.0 for $MgCNi_3$. In other words, the (1 0 0) peak clearly dominates over the (1 1 0) one for the carbon-rich compounds. This trend in R is a useful guideline and could possibly help to evaluate the quality of samples in future experiments, in particular if a comparison to a spectrum of a stoichiometric sample (e.g., $MgCNi_3$) is available.

Applying these results to the x-ray data of Dong *et al.*[5] we find another hint that the $AlCNi_3$ sample might be carbon deficient. While in the spectrum of $MgCNi_3$, which can be considered as stoichiometric, the (1 0 0) peak is clearly dominant, in the spectrum of $AlCNi_3$ it is not. It has a higher intensity than the (1 1 0) peak, but much less pronounced than one would expect from a comparison to $MgCNi_3$. From the viewpoint of our calculations, R should be similar for $AlCNi_3$ and $MgCNi_3$. Since it is not stated explicitly in Ref. 5 we have to assume that both measurements were performed on the same equipment. Thus one can directly compare the spectra and deviations between our calculations and the measurements should no longer play a role. A similar analysis for $GaCNi_3$ is much harder because the spectrum presented in Ref. 4 is rather noisy. Moreover, no comparison to a stoichiometric sample (e.g., $MgCNi_3$) is given.

In conclusion, our full-potential DFT calculations employing both the LDA and the GGA clearly show that stoichiometric $AlCNi_3$ and $GaCNi_3$ in the cubic antiperovskite structure are nonmagnetic metals with a low Stoner enhancement factor and energetically far away from a magnetic ground state. However, the DOS at E_f increases about linearly when the carbon concentration is lowered, strongly enhancing the tendency toward magnetism. A comparison of our calculated lattice constants with some older, experimentally determined ones[6] shows that the GGA is much better suited for a proper description of these compounds than the LDA. Moreover, a comparison of calculated x-ray spectra for samples with and without carbon shows a change in the relative peak intensity between the (1 0 0) and the (1 1 0) peaks, caused by the presence of carbon. In future experiments this could be used to roughly estimate the sample quality. Taking all the above results into consideration we also have evidence that some recent measurements[4,5] on $GaCNi_3$ and $AlCNi_3$ were performed on carbon-deficient samples. Both times tendencies toward magnetism were found, namely, strong electron-electron correlations in $GaCNi_3$ and weak ferromagnetism in $AlCNi_3$, which clearly were absent in our calculations. In future experimental work it is important to put great emphasis on the correct carbon stoichiometry. A controlled reduction of x in TC_xNi_3 with $T=$Al and Ga would be desirable, in particular due to the interesting physical properties at $x\approx 0$.

[1] T. He *et al.*, Nature (London) **411**, 54 (2001).

[2] M. D. Johannes and W. E. Pickett, Phys. Rev. B **70**, 060507(R) (2004).

[3] M. S. Park, J. S. Giim, S. H. Park, Y. W. Lee, S. I. Lee, and E. J. Choi, Semicond. Sci. Technol. **17**, 274 (2004).

[4] P. Tong, Y. P. Sun, X. B. Zhu, and W. H. Song, Phys. Rev. B **73**, 245106 (2006).

[5] A. F. Dong, G. C. Che, W. W. Huang, S. L. Jia, H. Chen, and Z. X. Zhao, Physica C **422**, 65 (2005).

[6] J. B. Goodenough and M. Longo, in *Magnetic and Other Properties of Oxides and Related Compounds*, edited by K.-H. Hellwege and A. M. Hellwege, Landolt-Börnstein–Group III Condensed Matter, New Series, Vol. 4, Part A (Springer-Verlag, Berlin, 1970), pp. 266–269.

[7] P. Eckerlin and H. Kandler, in *Structure Data of Elements and Intermetallic Phases*, edited by K.-H. Hellwege and A. M. Hellwege, Landolt-Börnstein–Group III Condensed Matter, New Series, Vol. 6 (Springer-Verlag, Berlin, 1971), pp. 94–108.

[8] C. M. I. Okoye, Solid State Commun. **136**, 605 (2005).

[9] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981).

[10] M. Sieberer, S. Khmelevskyi, and P. Mohn, Phys. Rev. B **74**, 014416 (2006).

[11] Computer code FLAIR (2006), http://www.uwm.edu/~weinert/flair.html

[12] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[13] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[14] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[16] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, New York, 1958).

[17] G. Y. Guo, Y. K. Wang, and L.-S. Hsu, J. Magn. Magn. Mater. **239**, 91 (2002).

[18] D. J. Singh and I. I. Mazin, Phys. Rev. B **64**, 140507(R) (2001).

[19] H. Rosner, R. Weht, M. D. Johannes, W. E. Pickett, and E. Tosatti, Phys. Rev. Lett. **88**, 027001 (2002).

[20] S. B. Dugdale and T. Jarlborg, Phys. Rev. B **64**, 100508(R) (2001).

[21] F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).

[22] G. L. Krasko, Phys. Rev. B **36**, 8565 (1987).

[23] F. R. de Boer, C. J. Schinkel, J. Biesterbos, and S. Proost, J. Appl. Phys. **30**, 1049 (1969).

[24] A. Aguayo, I. I. Mazin, and D. J. Singh, Phys. Rev. Lett. **92**, 147201 (2004).

[25] Computer code POWDERCELL (Bundesanstalt für Materialforschung und -prüfung, 2006), http://www.bam.de/de/service/publikationen/powder_cell.htm