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Structural discontinuity in the hexagonal *RT*Al compounds: Experiments and density-functional theory calculations

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An anomalous behavior of the lattice parameters is reported for *RT*Al and $R(T,T')$Al compounds, with *R* a rare-earth element and *T* and T' transition metals or Cu. In these compounds, which crystallize in the hexagonal ZrNiAl-type of structure, an abrupt transition in the temperature or composition dependence of the lattice constants *a* and *c* is observed with the common feature that values of the c/a ratio around 0.565–0.575 are generally not realized. Total-energy calculations based on density-functional theory show the occurrence of two close energy minima, which explains the observed structural instability and the associated transitions.

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I. INTRODUCTION

The ternary *RTX* compounds, which consist of a rare-earth element (*R*), Cu or a transition metal (*T*), and a *p*-metal (*X*) with an unfilled *p* shell of electrons, from the IIIB, IVB, or VB group of the Periodic Table, form a relatively large group. They crystallize in various structures, of which the most usual are the orthorhombic TiNiSi-type structure, the hexagonal AlB_2-type structure, and the hexagonal ZrNiAl-type structure (see Fig. 1). The compounds studied in the present work belong to the latter group and their interesting electronic and magnetic properties have been the subject of many studies (see, e.g., Refs. 1–5). Most of these compounds exhibit interesting magnetic behavior at low temperatures, often with rather complex ordered magnetic structures.

The present paper is devoted to the identification and investigation of an unusual structural phase transition with a general validity in the very large group of 111 rare-earth intermetallic compounds (*RTX*) with the hexagonal ZrNiAl-type crystal structure. A structural transition has been observed in these compounds if the temperature is varied, and in quasiternary $R(T,T')X$ compounds if the T-T' ratio is varied. These transitions consist of a considerable change of the lattice parameters *a* and *c* without changing the ZrNiAl-type structure. Since the parameters *a* and *c* change in the opposite way, the transition involves a large change of the c/a ratio (~2%), but the unit-cell volume is practically unchanged. As shown by Merlo *et al.*,[6] discontinuities exist in the behavior of the lattice parameters *a* and *c* of *R*NiAl compounds if they are plotted as a function of the atomic number *Z* of the constituting *R* element. Whereas the lanthanide contraction gives rise to a general smooth decrease of both *a* and *c* with increasing *Z*, the value abruptly increases at 300 K upon going from SmNiAl to GdNiAl (EuNiAl is not stable). Simultaneously, the parameter *c* exhibits a sudden decrease. In Fig. 2, the behavior of the *R*NiAl series is shown in the c/a representation, together with the *R*PdAl and *R*CuAl series. Although the ZrNiAl-type structure is conserved, a distinct change of the c/a ratio and a common gap between the "low c/a" values and the "high c/a" values are observed between R=Gd and Sm for the *R*NiAl (Ref. 7) and *R*PdAl (Ref. 8) series. This gap of c/a values that is not realized extends from ~0.562 to ~0.573. The *R*CuAl (Ref. 9) series neither show such an effect nor show the "forbidden" c/a values. The results in Fig. 2 suggest that similar discontinuities in *a* and *c* may be expected in the compounds at the boundary of the c/a gap if external parameters such as temperature or pressure are varied.

The first observation of this type of structural transition as a function of temperature has been reported for TbNiAl.[10] After this, the transition was also found in GdNiAl and studied in detail on a polycrystalline material.[6] These findings have been confirmed by studying a single crystal.[11] Later, the transition has also been observed for TbPdAl (Ref. 12) and GdPdAl.[13,14] The common features of the structural transition in all the above four compounds are that they are in the high c/a state at low temperatures and that, with increasing temperature, the low c/a phase appears, the amount of which gradually increases with increasing temperature at the expense of the high c/a phase. The width of the temperature interval in which the two phases coexist ranges, depending on the compound, from zero up to 25 K. The c/a values of the gap range in which these compounds are not stable roughly range between 0.565 and 0.575, which is in reasonable agreement with the values for the series of compounds displayed in Fig. 2.

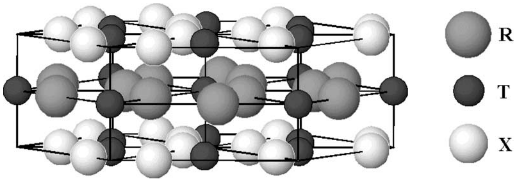

FIG. 1. The hexagonal ZrNiAl-type structure adopted by the studied *RT*Al compounds.

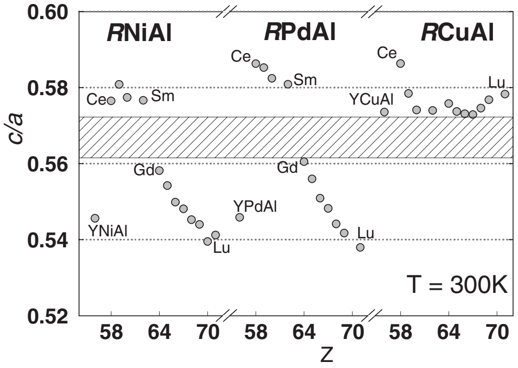

FIG. 2. Development of the c/a ratio in the RNiAl (Ref. 7), RPdAl (Ref. 8), and RCuAl (Ref. 9) series. The individual points in each series correspond to different rare-earth elements in the sequence Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu. Data for compounds with R=Eu are not available.

Similar to the transition as a function of temperature, a large c/a jump has also been observed as a function of the Ni-Cu concentration ratio in several pseudoternary $R\mathrm{Ni}_{1-x}\mathrm{Cu}_x\mathrm{Al}$ series, first for R=Tb[10] and later also for R=Er[15] and Dy.[16] For the different constituting rare-earth elements, the c/a change occurs at different Cu concentrations but at the same c/a values; the c/a values that are not realized always fall in the interval between 0.558 and 0.575.

The combination of all the above presented results suggests the existence of a specific "forbidden range" of c/a values—between ≈0.565 and ≈0.575—in which compounds cannot crystallize in the ZrNiAl-type structure.[16,17] The systems $\mathrm{TbPd}_{1-x}\mathrm{Ni}_x\mathrm{Al}$ and $\mathrm{TbNi}_{1-x}\mathrm{Cu}_x\mathrm{Al}$ should be mentioned as behaving exceptionally in the sense that, for higher x values, the change from the high c/a phase to the low c/a phase takes place in a gradual way as temperature increases, without the coexistence of the two phases and without any c/a gap.[17]

In the present paper, we give a brief summary of reported results related to the structural transition introduced above and also present additional results mainly concerning compounds having a c/a ratio close to the gap values. In addition, calculations of the total energy are presented, which explain the experimental results.

II. EXPERIMENT

The investigated materials have been prepared by arc-melting stoichiometric amounts of the pure elements (with a purity of 3*N* for the rare earths, 4*N*5 for Ni and Pd, and 5*N* for Cu and Al, respectively) in a mono-arc furnace under the protection of an Ar atmosphere (6*N*), using the furnaces at the Department of Condensed Matter Physics (DCMP) in Prague and at NIMS, Tsukuba. The x-ray diffraction (XRD) experiments were performed by using a Siemens diffractometer (DCMP), a Rigaku diffractometer (NIMS) with a low-temperature option, operating in the temperature range from 8 to 320 K, and a Nonius powder diffractometer [with a 120° position-sensitive (bended) Inel detector], which is able to operate at temperatures up to 900 °C (WZI, Amsterdam). All of the mentioned instruments are working with conventional Bragg–Brentano geometry. Cu $K\alpha_{1,2}$ radiation was used for the XRD experiments in all cases.

Specific-heat experiments were performed by using a Physical Property Measurement System (PPMS-14T, Quantum Design) instrument, which uses the two-τ relaxation method to determine the heat capacity. Measurements were done on polycrystalline samples; in the case of GdNiAl, approximately 15 mg. For the measurement of the heat capacity of TbNiAl, we used a pellet made by mixing TbNiAl powder with silver powder in the weight ratio 1:1. We used this method to improve the thermal contact of the sample with the sample holder platform and to solve the problem that a sample of the pure compound detaches from the platform when the compound passes through the phase transition around 110 K.

The magnetization of the TbNiAl single crystal was measured in a superconducting quantum interference device magnetometer (Quantum Design) in the temperature range of 1.8–300 K.

III. CRYSTAL STRUCTURE

The hexagonal ZrNiAl-type structure with the space group $P\bar{6}2m$ (No. 189) is depicted in Fig. 1. It consists of two alternating types of basal plane layers, perpendicular to the c axis and changing periodically in the sequence $ABAB$. One type of the layers contains the rare earth (R) and one-third of the transition-metal (T) atoms. These layers are separated by nonmagnetic layers containing the p-metal (X) atoms and the remaining two-thirds of the transition-metal atoms (T). The atomic coordinates are as follows:

$3R$ ($3g$): $(X_R, 0, 1/2)$, $(0, X_R, 1/2)$, $(-X_R, -X_R, 1/2)$,
$1T$ ($1b$): $(0, 0, 1/2)$,
$3X$ ($3f$): $(Y_X, 0, 0)$, $(0, Y_X, 0)$, $(-Y_X, -Y_X, 0)$,
$2T$ ($2c$): $(1/3, 2/3, 0)$, $(2/3, 1/3, 0)$.

The internal parameters X_R and Y_X are almost the same for all compounds with the ZrNiAl-type structure: $X_R \approx 0.58$, $Y_X \approx 0.2$. When varying the temperature for a given composition or when varying the composition at a given temperature, these parameters do not change within the usual experimental accuracy, except for a very slight change around the temperature of transition in several cases. Nevertheless, this change is at least an order of magnitude smaller than the relative change in the lattice parameters and does not affect the evolution of the lattice parameters. Therefore, we will not deal with the internal parameters further. The structural transition has been observed in the temperature dependence of the lattice parameters or upon the substitution of another element in a given RTX compound. Another possibility may be to induce the transition by applying external pressure. However, until the present, only the two studies have been carried out or reported in literature and a pressure induced transition has not yet been realized.

IV. RESULTS

A. Structural transformation with temperature variation

Examples of the structural transition are presented in Fig. 3, including other detailed results obtained for TbNiAl

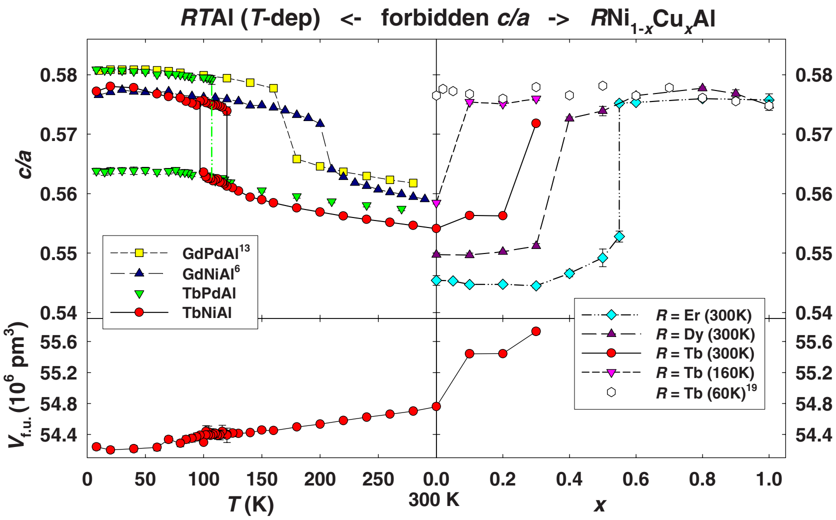

FIG. 3. (Color online) Demonstration of the forbidden c/a ratio values for RTAl compounds, realized either by variation of the temperature (left part) or by substitution (right part). The example of a monotonous evolution of the volume of the Tb based compounds is displayed to demonstrate the contradiction between the behavior of c/a and the volume. The data for the GdNiAl and GdPdAl (left upper part) were estimated from the figures in Refs. 6 and 13; the values for the $TbNi_{1-x}Cu_xAl$ series at 60 K were estimated from the figure in Ref. 19.

and the pseudoternary $TbNi_{1-x}Cu_xAl$ compounds. Between 95 and 120 K, the lattice parameters a and c of TbNiAl exhibit a discontinuity (see Fig. 4), with both parameters changing in opposite sense, so that the volume does not seem to be much affected by the transition (Fig. 3). Moreover, a coexistence of the high c/a and low c/a phases is observed. The two phases coexist in a temperature range of 25 K ($95\text{ K} < T < 120\text{ K}$; see Fig. 4). Another studied compound, $ErNi_{0.45}Cu_{0.55}Al$, exhibits the coexistence of two phases from the lowest studied temperature of 8 K up to high temperatures of several hundred Kelvin and becomes a single phase above ~493 K (Fig. 5). It is worthy to mention that this effect is reversible, i.e., after cooling down below 493 K, the $ErNi_{0.45}Cu_{0.55}Al$ separates into two phases again. The XRD patterns with focus on the reflections exhibiting splitting due to the presence of the two phases are displayed for the TbNiAl and $ErNi_{0.45}Cu_{0.55}Al$ compounds in Fig. 6. Other examples of compounds that exhibit the coexistence of two phases with the same hexagonal ZrNiAl-type structure are TbPdAl and $TbPd_{0.9}$ $Ni_{0.1}Al$,[12,17,18] and also $TbNi_{1-x}Cu_xAl$ with $x=0.1$ and 0.2, with the transition between 200 and 250 K (Fig. 4).

Besides the direct measurements of the lattice parameters by using XRD or neutron diffraction, we could also observe a change in the evolution of several other physical properties at temperatures close to the isostructural transition. Measurements of the temperature dependence of the specific heat of TbNiAl did not reveal observable anomalies corresponding to the change of the structural parameters (Fig. 7). The measurement was, nevertheless, indirectly affected by the structural discontinuity; the sample itself had a strong tendency to

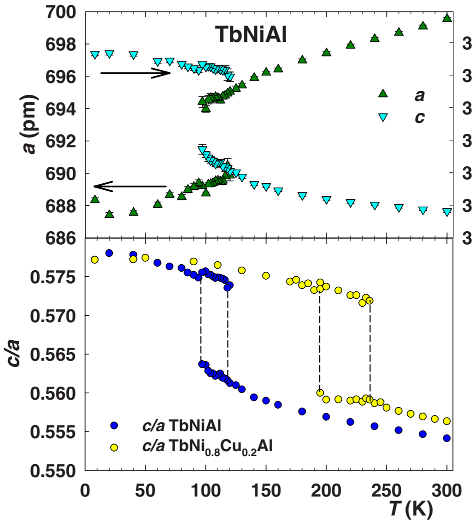

FIG. 4. (Color online) Temperature dependence of the unit-cell parameters a and c of TbNiAl and the c/a ratio in TbNiAl and $TbNi_{0.8}Cu_{0.2}Al$. In the overlapping area, a coexistence of both structural phases (high c/a and low c/a) is usually observed. The evolution of c/a values of $TbNi_{0.9}Cu_{0.1}Al$ is very similar to that of $TbNi_{0.8}Cu_{0.2}Al$.

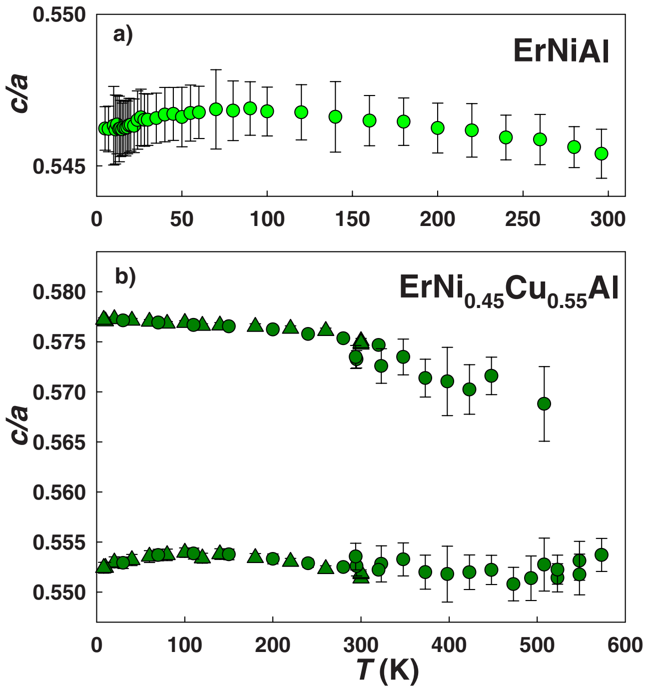

FIG. 5. (Color online) The temperature dependence of the c/a ratio in ErNiAl and $ErNi_{0.45}Cu_{0.55}Al$ compounds.

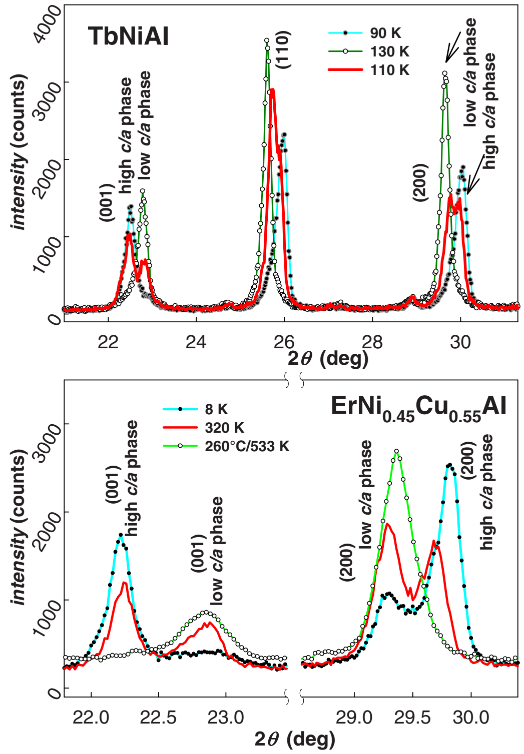

FIG. 6. (Color online) XRD patterns of compounds exhibiting two-phase coexistence. The patterns are focused on reflections that split most significantly in the coexistence region.

detach from the sample holder when passing through the critical temperature of 100 K. The specific-heat measurement on a polycrystalline (not annealed) GdNiAl sample reveals a small anomaly (see Fig. 7) at the temperature of crystallographic transition.

Results of measurements of the temperature dependence of the inverse magnetic susceptibility of a TbNiAl single crystal are presented in Fig. 8. The compound follows the Curie–Weiss law, but with a slight change of the effective magnetic moment μ_{eff} and the paramagnetic Curie temperature θ_p at around 160 K. Table I summarizes the values obtained from the fit of our data. A similar change of the effective magnetic moment was observed in TbPdAl,[12] GdNiAl,[6] and GdPdAl[13] around the temperature of the structural transition. A common feature of this effect is an increased value of the effective moment for temperatures below the structural transformation. An explanation of the effect was proposed by Merlo *et al.*[6] as a larger polarization of the conduction electrons in the paramagnetic region below the structural transformation due to the changed distances between the ions. An alternative explanation is related to a slight decrease in the Pd 4*d* peak in the x-ray photoemission spectroscopy (XPS) spectra[13,14] below the transition, possibly due to a stronger hybridization of the Pd 4*d* states with the almost empty Gd 5*d* and Al 3*p* states. We note that anomalies close to the isostructural transition were also reported for the electrical resistivity of GdPdAl[13] and GdNiAl[6,11] and for the XPS of GdNiAl.[20]

Although the substituted compounds $\mathrm{TbNi_{0.9}Cu_{0.1}Al}$ and $\mathrm{TbNi_{0.8}Cu_{0.2}Al}$ exhibit a similar behavior to TbNiAl, a higher substitution of Cu ($x \geq 0.3$) leads to a slightly different behavior; these compounds exhibit a continuous evolution of the lattice parameters and their c/a ratio passes through the forbidden zone (Fig. 9). A similar effect has been observed for $\mathrm{TbPd_{1-x}Ni_xAl}$ samples[17] with x=0.2, 0.5, and 0.8 (Fig. 9). In $\mathrm{TbNi_{0.7}Cu_{0.3}Al}$ and the $\mathrm{TbPd_{1-x}Ni_xAl}$ compounds with x=0.2–0.8, the type of the transition has

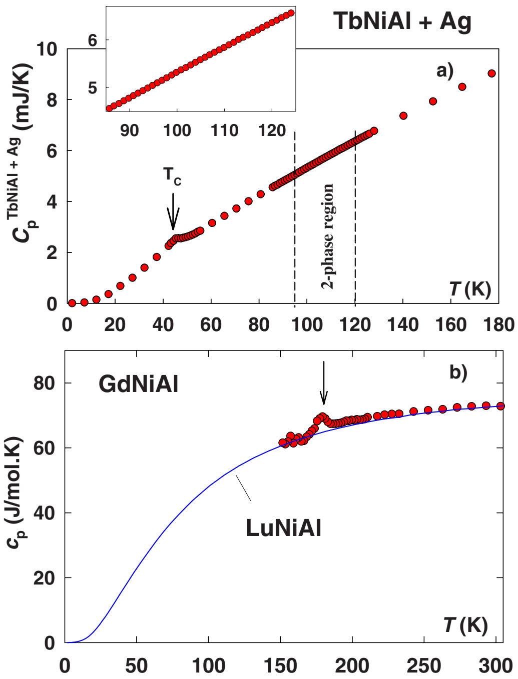

FIG. 7. (Color online) Temperature dependence of the heat capacity of TbNiAl and GdNiAl. Data for the nonmagnetic analog LuNiAl are displayed together with GdNiAl for a better estimation of the contribution to the structural transformation. The TbNiAl sample was measured only as a mixture with the silver powder (see Sec. II). As the TbNiAl/Ag ratio could not be precisely determined, we present only the heat capacity of the whole (TbNiAl+Ag) sample in mJ/K.

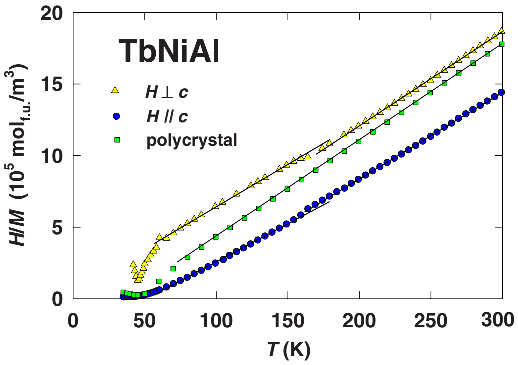

FIG. 8. (Color online) Inverse dc susceptibility of TbNiAl measured with the magnetic field applied along the c axis and perpendicular to it. Solid lines represent the Curie–Weiss law with μ_{eff} and θ_p parameters that differ in different temperature regions (see text). Polycrystalline data are shown as well, but no effect is observed to be similar to that measured on a single crystal.

TABLE I. Effective moments μ_{eff} and paramagnetic Curie temperatures θ_p of a TbNiAl single crystal. Different values are obtained in the temperature regions above and below 160 K.

Field direction	T region	μ_{eff} (μ_B)	θ_p (K)
$H \parallel a$	$T < 160$ K	10.37	−8.6
	$T > 160$ K	9.83	16.5
$H \parallel c$	$T < 160$ K	10.95	51.3
	$T > 160$ K	10.26	61.5

changed to second order. This will be further discussed below.

B. Structural transformation with changing composition

When inspecting in Fig. 3 the occurrence of the transition in the TbNi$_{1-x}$Cu$_x$Al series as a function of the Cu concentration, we observe a shift of the transition to lower Cu concentrations upon decreasing temperature. In the temperature range from 200 to 300 K, the discontinuity of the lattice parameters happens between $x=0.2$ and 0.3, whereas at temperatures from 120 to 200 K, it is shifted to concentrations between $x=0.0$ (TbNiAl) and 0.1. Below 90 K, there is no anomaly in the Cu concentration dependence, which is in accordance with the finding of Ehlers *et al.*[19] at 60 K (see Fig. 3). On the other hand, the ErNi$_{1-x}$Cu$_x$Al and DyNi$_{1-x}$Cu$_x$Al series exhibit the anomaly in the same Cu concentration region, i.e., between $x=0.5$ and 0.6 and between $x=0.3$ and 0.4 for Er and Dy, respectively, in the whole studied temperature range from room temperature (studied by XRD) down to 1.6 K (studied by neutron diffraction).[15,16]

Our interest in the effect of the transformation on the crystal field brought several additional results. An investigation of the crystal field levels in the ErNi$_{1-x}$Cu$_x$Al series revealed a change in the systematic evolution of the scheme in the range $0.5 < x < 0.6$,[21] which is just in accordance with the composition where the structure changes. Also, inelastic neutron scattering has been carried out to study the changes of the crystal field in the TbNiAl and TbPdAl compounds around the transition temperature. The results indicate no deviation from the systematic evolution of the peaks in the energy spectra around the temperature of the structural transformation.[22]

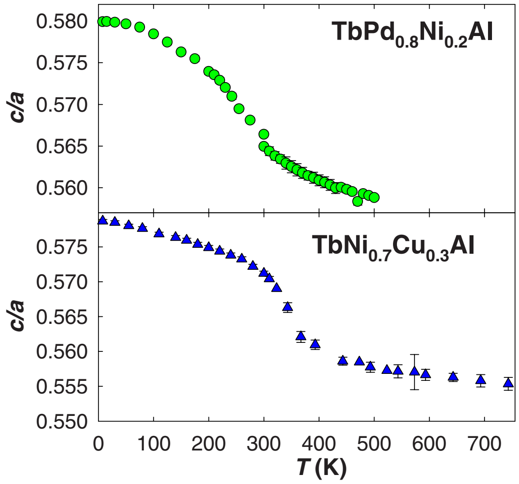

FIG. 9. (Color online) Temperature dependence of the c/a ratio of TbPd$_{0.8}$Ni$_{0.2}$Al and TbNi$_{0.7}$Cu$_{0.3}$Al measured up to 470 °C (743 K) and 227 °C (500 K), respectively. A second-order type transition is visible around the forbidden c/a values.

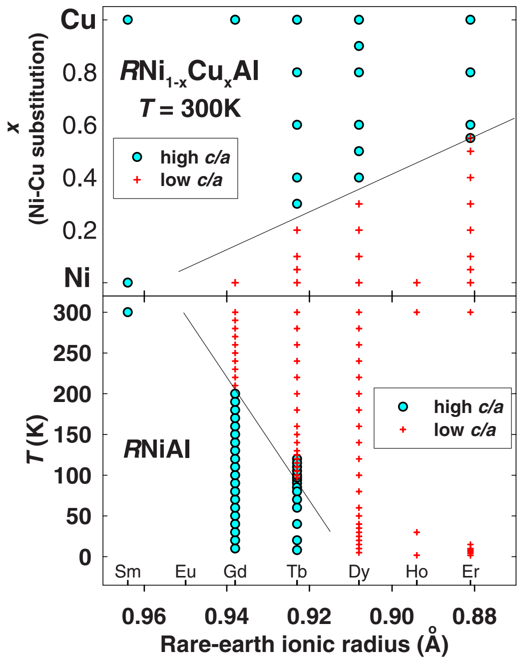

FIG. 10. (Color online) Systematic evolution of the boundary between RNi$_{1-x}$Cu$_x$Al compounds containing a high c/a and a low c/a ratio. The data were taken for SmNiAl (Ref. 6), SmCuAl (Ref. 24), GdNiAl (Ref. 6), GdCuAl (Ref. 24), TbNi$_{1-x}$Cu$_x$Al (Ref. 10), DyNiAl-Tdep (Ref. 25), DyNi$_{1-x}$Cu$_x$Al (Ref. 16), HoNiAl (Ref. 26), and ErNi$_{1-x}$Cu$_x$Al (Ref. 15).

Another case of a nonlinear variation of the lattice parameters by varying the composition was observed at room temperature for the Ce$_{1-x}$Y$_x$PdAl series (which represents a different type of substitution).[23] Also in this system, two coexisting phases (with the phases belonging above and below the transition, respectively) are found in the critical region of $0.4 \leq x \leq 0.6$, similar to the coexistence in the compounds presented above (TbNiAl, ErNi$_{0.45}$Cu$_{0.55}$Al, etc.).

The boundary between compounds with the high c/a and low c/a ratios systematically follows the composition of the compounds at a given temperature. Figure 10 displays this boundary for a special case of the Ni-Cu substitution at room temperature, together with the temperature evolution for RNiAl compounds. A notable feature in this figure and also in Fig. 3 is the fact that the discontinuity in the evolution of the lattice parameters is not a direct matter of volume change, i.e., one cannot decide whether the boundary will be reached by increasing or decreasing the volume. In order to explain this, we focus, for example, on the compounds with $R=$Tb. When moving from TbCuAl to TbNiAl in the

$\mathrm{TbNi}_{1-x}\mathrm{Cu}_x\mathrm{Al}$ series (i.e., from $x=1.0$ down to $x=0.0$) at room temperature, the structural discontinuity occurs between $x=0.3$ and $x=0.2$. At this concentration, the c/a ratio changes from the high c/a ($c/a_{0.3}\approx 0.572$) to the low c/a ($c/a_{0.2}\approx 0.556$) and the volume change is negative (the volume decreases). On the other hand, upon cooling TbNiAl (i.e., further decrease of the volume, according to the lower part of Fig. 3), the c/a ratio exhibits a sudden change from the low c/a to the high c/a at approximately 110 K ($c/a_{125\text{ K}}\approx 0.561$; $c/a_{94\text{ K}}\approx 0.575$), while the volume still decreases. The discontinuity in the evolution of the ratio of structural parameters c/a does not affect the linearity of the volume evolution in the other series as well.

C. Total-energy calculations

To theoretically investigate this interesting phase transition, we have performed first principles electronic structure calculations based on the density-functional theory. We used the full potential linearized augmented plane wave method [WIEN2K][27] and the local-density approximation.[28] First, we calculated the equilibrium c/a values for the three compounds LuNiAl, LuCuAl, and LuPdAl and, in all three cases, the obtained c/a values, which are very close to the reported experimental values. This correspondence motivated us to perform the calculations on the large c/a mesh.

We have performed a series of total-energy calculations for the $\mathrm{ErNi}_{1-x}\mathrm{Cu}_x\mathrm{Al}$ family of compounds to investigate the competition between the two phases observed at different concentrations of Ni and Cu. Non-spin-polarized calculations including spin-orbit coupling were performed for a mesh of six values of the lattice parameter a and seven values of the lattice parameter c. A calculation of the total-energy surface for ErNiAl ($x=0$) reveals two clear minima [Fig. 11(a)] with similar depth (the total-energy difference is less than 2.5 meV/f.u.). These minima correspond to c/a ratios of 0.55 and 0.57, which is in good agreement with experimental observations. An increase in the Cu content to $x=0.5$ gradually suppresses the depth of the minimum corresponding to the lower c/a ratio [Fig. 11(b)]. At $x=0.55$, this minimum completely disappears and only the minimum with $c/a=0.57$ remains. This tendency of suppressing the smaller c/a minimum (i.e., the low c/a phase) with increasing Cu content is also in agreement with experimental observations.

V. DISCUSSION

The observed structure transformation occurs between two phases that both possess the same ordered ZrNiAl-type structure. At the transformation temperature, the lattice parameters a and c change in the opposite way, giving rise to a transformation between the high c/a phase and the low c/a phase. Due to the opposite changes of a and c, the volume change at the transition is small. As has been established for GdPdAl,[14] the phase transformation involves, apart from the changes in the lattice parameters a and c and the concordant changes of the distances between neighboring atoms, also a slight change of the atomic coordinates X and Y. The key property is that, after such a change, the nearest neighbors of the rare-earth ions (carrying the magnetic moment) are still the ones within the basal plane. It may be expected that the magnetic properties of the material would dramatically change if the isostructural transition would involve a change of the R-R nearest neighbors from the in-plane to the intraplane ones. We recall that the nearest R-R neighbors along the c direction exist, e.g., in several RPdIn compounds.[29] Altogether, since the ordered ZrNiAl-type structure is retained and the overall coordination of the atoms remains unchanged, the small changes in atomic positions will lead to

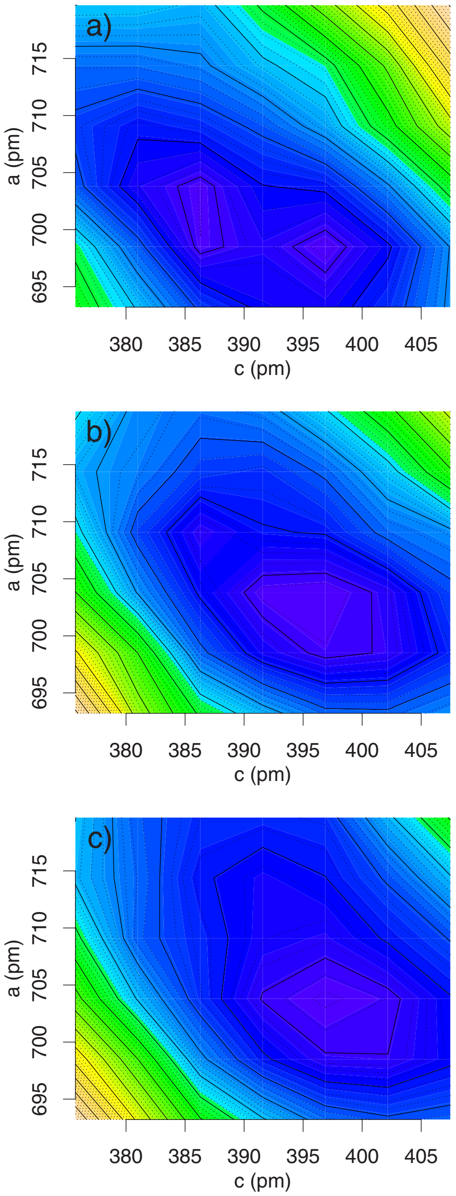

FIG. 11. (Color online) Results of the total-energy calculations as a function of the lattice constants a and c. In the calculation, the electronic parameters of (a) ErNiAl, (b) $\mathrm{ErNi}_{0.5}\mathrm{Cu}_{0.5}\mathrm{Al}$, and (c) $\mathrm{ErNi}_{0.45}\mathrm{Cu}_{0.55}\mathrm{Al}$ were used. The total energy was evaluated for a 6×7 point mesh. The solid contours connect points with equal energy with a spacing of 10 meV. Light colors (green and yellow) denote higher energies and dark colors (blue) denote lower energies. Two energy minima with c/a ratios of approximately 0.55 and 0.57 are clearly visible.

only slightly different atomic distances and the associated bond lengths. Therefore, the energy effect involved in the structural transformation cannot be expected to be very large.

The experimental results show that the structural transformation between the high c/a phase and the low c/a one is hysteretic and suggest that the phase transition is first order, a transition that is governed by nucleation and growth. However, the temperature interval in which the phase transition takes place, and in which the two phases coexist, is generally quite large, too large to be simply ascribed to the first-order character of the transition. The very sluggish transition in which, with increasing temperature, the low c/a phase gradually appears and increases in amount at the expense of the high c/a phase strongly suggests that in some parts of the crystal the transition takes place at a lower temperature than in other parts. One may speculate that the large observed temperature hysteresis of the transformation may be caused by the presence of lattice imperfections or strains in the crystallites and that in high-quality samples, in the ideal case of thermodynamic equilibrium, a much reduced hysteretic behavior would be expected.

There is clear evidence, indeed, that the transition is affected by the quality of the sample. As an example, we consider the results on GdNiAl. In a polycrystalline sample of this compound, the transition was observed as a smooth transition (including values in the c/a gap),[25] whereas for a single crystal of higher quality, a sharp transition was observed without c/a values in the gap.[11] By comparing the annealed and as-cast TbPdAl samples,[12,17] a similar conclusion on a narrower coexistence region in a better-quality sample can be drawn. Also, the anomalies observed at around 160 K in the magnetic susceptibility of a TbNiAl single crystal and their absence in a polycrystalline sample corroborate this conclusion (see Table I and Fig. 8). Furthermore, it seems that a higher transition temperature is indicative of a better sample quality—the transition in GdNiAl was observed at around 180 K by Daniš *et al.*,[25] but at temperatures above 200 K by Merlo *et al.*[6] and Jarosz *et al.*[11] The width of the coexistence of both crystallographic phases is a further parameter influenced by sample quality—a better quality results in a narrower coexistence region, as seen, for instance, when we compare the results on the annealed and unannealed TbPdAl.[12,17]

In the case of the $\mathrm{TbPd}_{1-x}\mathrm{Ni}_x\mathrm{Al}$ system, a certain preferential occupation of the T sites by Ni/Pd atoms has been observed, but still with a large degree of randomness.[30] Taking into account the relatively different sizes of the Ni and Pd atoms leads to a variable geometry of the bonds. Forbidden c/a values can then be realized if this effect becomes significant, i.e., if the substitution is higher than about 10%.[17] The same holds for the $\mathrm{Ce}_{1-x}\mathrm{Y}_x\mathrm{PdAl}$ compounds, for a substitution higher than about 20%.[23] On the other hand, Ni-Cu substitution in $R(\mathrm{Ni,Cu})\mathrm{Al}$ systems concerns the substitution of atoms with similar size. No preferential occupation is observed in these compounds and a sharp c/a jump occurs like in many unsubstituted materials.

In the following, we will make a quantitative consideration of the values of the enthalpies and entropies involved in the phase transformation between the high c/a and low c/a phases. If the two phases are in thermodynamic equilibrium at the transformation temperature T^{tr}, they have the same values of the free enthalpy or Gibbs free energy, so that $\Delta G=0$. From this, we show the following relationship between the enthalpy of transformation ΔH^{tr} and the entropy of transformation ΔS^{tr} at T^{tr}:

$$\Delta H^{\mathrm{tr}} = T^{\mathrm{tr}} \times \Delta S^{\mathrm{tr}}. \qquad (1)$$

Since both phases involved are atomically ordered at T^{tr}, the contribution to ΔS^{tr} that is due to atomic disorder, the so-called configurational entropy, will be negligible and ΔS^{tr} will mainly consist of vibrational entropy. This is in contrast to the cases (Cu-Au, Pd-Ni, etc.) where the low-temperature phase is atomically ordered and the transformation to an atomically disordered structure takes place. Unfortunately, in the compounds investigated, the transition is usually smeared out over a wide temperature range, which does not facilitate an accurate experimental determination of the heat of transformation ΔH^{tr} or the entropy of transformation ΔS^{tr}. As can be seen in the specific-heat measurements of TbNiAl in Fig. 7(a), there is even no anomalous behavior visible at all in the relevant temperature interval. In GdNiAl, however, the transformation takes place in a relatively small temperature range and a clear anomaly in the specific heat is found [Fig. 7(b)]. From this anomaly, only a lower limit of the transformation enthalpy ΔH^{tr} of 0.2 kJ/mol can be derived. If we take $T^{\mathrm{tr}}=100$ K as a typical value, the lower limit of the transformation entropy ΔS^{tr} is equal to about 2 J/Kmol.

Since structural phase transitions from one atomically ordered state to another are not very frequently encountered in intermetallic compounds and no information on the values of ΔH^{tr} and ΔS^{tr} involved in such transformations is available in literature, it is difficult to compare the values observed for GdNiAl with other experimental data. The only available information on enthalpy and entropy changes in phase transformations between atomically ordered structures concerns a number of pure metals that exhibit allotropy, for instance, Mn, Fe, Co, Th, and Ca.[31] In these pure metals, the ΔH^{tr} values range from 0.4 to 2.7 kJ/mol and the ΔS^{tr} values from 0.6 to 2.3 J/K mol. The ΔS^{tr} value of GdNiAl falls reasonably within the range of ΔS^{tr} values of the pure metals, whereas ΔH^{tr} is clearly smaller. Apart from the fact that $\Delta H^{\mathrm{tr}}=0.2$ kJ/mol is only a rough estimate of the lower limit, a small value of ΔH^{tr} may be expected since a structural change is very minor, with the crystal structure basically being retained, whereas in phase transitions in the pure metals, which are between two different crystal structures, the atomic distances and coordination, and, hence, the atomic bonding, change significantly.

The primary aim of the total-energy calculations that have been performed on the $\mathrm{ErNi}_{1-x}\mathrm{Cu}_x\mathrm{Al}$ system was to investigate whether they provide two energy minima, which are close in energy, and also to study the relative evolution of these energy minima with increasing Cu contents. The calculation for ErNiAl [Fig. 11(a)], indeed, provides two energy minima with a difference of less than 7.5 meV/atom, which corresponds to an upper limit of ΔH^{tr} of 0.7 kJ/mol. This upper limit of ΔH^{tr} belongs to the lower values in the range of ΔH^{tr} values (0.4–2.7 kJ/mol) observed for structural transitions in a number of pure metals which, as discussed above, can be understood. Although, fundamentally, the calculated two energy minima are in very satisfactory qualitative agreement with the experimental findings, there are still points at which the calculations deviate from experiment. Particularly, the coexistence of the two minima is expected at around $x=0.5$ and not at $x=0.0$, where only the $c/a=0.55$ phase is observed. More accurate calculations, which would include spin polarization and a more careful treatment of the notoriously difficult $4f$ electrons (e.g., with the use of the LDA+U method, see Ref. 27 and references therein) might improve the agreement with experiment, but go beyond the scope of the present qualitative (or semiquantitative) theoretical study. What concerns the origin of the presence of two energy minima in these systems, based on our calculations, appears to be a relativistic effect. A calculation of the total-energy surface for $x=0$ (not shown) without the spin-orbit interaction for the valence states does not display two minima, but only one broad elliptical minimum. The introduction of the spin-orbit interaction itself into the calculations leads to a different description of the $5p$ states ($5p_{1/2}$ has a nonzero density at the atom-nucleus position), which influences the density of valence electrons, particularly their spatial distribution and, in turn, the bonding properties of the system. A more detailed analysis of these effects is planned.

Finally, we discuss the observation that in some quasiternary systems, such as $TbPd_{0.8}Ni_{0.2}Al$ (Fig. 9), $TbNi_{0.7}Cu_{0.3}Al$ (Fig. 9), and $Ce_{1-x}Y_xPdAl$,[23] the structural transition is not of first order. Although, also in these systems, the high c/a phase is stable at low temperatures (or low content of Y for $Ce_{1-x}Y_xPdAl$) and the low c/a phase at high temperatures (or high content of Y for $Ce_{1-x}Y_xPdAl$), the structural transition gradually develops, like second order, involving intermediate c/a values. The observation (Fig. 9) that the change into a gradual transition with intermediate c/a values occurs in compounds with a larger doping content (20% Ni substituted for Pd in TbPdAl and 30% Cu for Ni in TbNiAl) strongly indicates that it is related to the atomic disorder in the quasiternary alloys. Disorder will give rise to a local variation of the atomic coordinations and the atomic distances. This will lead to a spectrum of ΔH^{tr} values and, associated with this, the observed smearing out of the structural transition.

VI. CONCLUSIONS

It has been shown that the isostructural transition observed in a number of compounds with the ZrNiAl-type hexagonal structure has a general validity. The c/a values from 0.565 to 0.575 represent a forbidden region that is skipped during the transition. The total-energy calculations based on density-functional theory reveals the occurrence of two energy minima, which can explain the observed isostructural transformation between two phases with the c/a values below and above the forbidden range. Thermodynamic aspects of the occurrence of the isostructural transition are thoroughly discussed.

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[1] H. Fujii, T. Inoue, Y. Andoh, T. Takabatake, K. Satoh, Y. Maeno, T. Fujita, J. Sakurai, and Y. Yamaguchi, Phys. Rev. B **39**, 6840 (1989).

[2] D. T. Adroja, S. K. Malik, B. D. Padalia, and R. Vijayaraghavan, Phys. Rev. B **39**, 4831 (1989).

[3] G. Ehlers and H. Maletta, Z. Phys. B: Condens. Matter **101**, 317 (1996).

[4] G. Ehlers, C. Ritter, A. Krutjakow, W. Miekeley, N. Stüsser, Th. Zeiske, and H. Maletta, Phys. Rev. B **59**, 8821 (1999).

[5] O. Garlea, E. Morosan, S. L. Bud'ko, J. L. Zarestky, P. C. Canfield, and C. Stassis, J. Appl. Phys. **95**, 6921 (2004).

[6] F. Merlo, S. Cirafici, and F. Canepa, J. Alloys Compd. **266**, 22 (1998).

[7] P. Javorský, Ph.D. thesis, Charles University, Prague, (1997).

[8] F. Hulliger, J. Alloys Compd. **218**, 44 (1995).

[9] N. C. Tuan, Ph.D. thesis, Charles University, Prague, (1992).

[10] G. Ehlers, Ph.D. thesis, Technische Universität, Berlin, 1996.

[11] J. Jarosz, E. Talik, T. Mydlarz, J. Kusz, H. Böhm, and A. Winiarski, J. Magn. Magn. Mater. **208**, 169 (2000).

[12] A. Dönni, H. Kitazawa, P. Fischer, and F. Fauth, J. Alloys Compd. **289**, 11 (1999).

[13] E. Talik, M. Skutecka, J. Kusz, H. Böhm, J. Jarosz, T. Mydlarz, and A. Winiarski, J. Alloys Compd. **325**, 42 (2001).

[14] J. Kusz, H. Böhm, E. Talik, M. Skutecka, and J. Deniszczyk, J. Alloys Compd. **348**, 65 (2003).

[15] J. Prchal, P. Javorský, V. Sechovský, M. Dopita, O. Isnard, and K. Jurek, J. Magn. Magn. Mater. **283**, 34 (2004).

[16] J. Prchal, P. Javorský, S. Daniš, K. Jurek, and J. Dlouhý, Czech. J. Phys. **54**, 315 (2004).

[17] J. Prchal, H. Kitazawa, T. Furubayashi, P. Javorský, K. Koyama, and V. Sechovský, Physica B **378–380**, 1102 (2006).

[18] A. Dönni, L. Keller, H. Kitazawa, J. Prchal, and P. Fischer, J. Alloys Compd. (in press) (DOI: 10.1016/j.jallcom.2007.10.043).

[19] G. Ehlers, D. Ahlert, C. Ritter, W. Miekeley, and H. Maletta, Europhys. Lett. **37**, 269 (1997).

[20] J. Jarosz and E. Talik, J. Alloys Compd. **317–318**, 385 (2001).

[21] P. Javorský, P. Daniel, E. Šantavá, and J. Prchal, J. Magn. Magn. Mater. **316**, E400 (2007).

[22] P. Javorský, J. Prchal, and D. Adroja, Solid State Commun. **146**, 21 (2008).

[23] J. Prchal, H. Kitazawa, and O. Suzuki, J. Alloys Compd. **437**, 117 (2007).

[24] P. Javorský, L. Havela, V. Sechovský, H. Michor, and K. Jurek, J. Alloys Compd. **264**, 38 (1998).

[25] S. Daniš, P. Javorský, and D. Rafaja, J. Alloys Compd. **345**, 10

(2002).
[26] P. Javorský, H. Sugawara, D. Rafaja, F. Bourdarot, and H. Sato, J. Alloys Compd. **323–324**, 472 (2001).
[27] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2K* (Technische Universität Wien, Austria, 2001).
[28] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[29] Ł. Gondek, S. Baran, A. Szytuła, D. Kaczorowski, and J. Hernández-Velasco, J. Magn. Magn. Mater. **285**, 272 (2005).
[30] P. Javorský, J. Prokleška, O. Isnard, and J. Prchal, J. Phys.: Condens. Matter **20**, 104223 (2008).
[31] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements* (American Society for Metals, Ohio, 1973).