THE SPECIFIC HEATS OF LaNi$_5$, GdNi$_5$ AND TbNi$_5$ COMPOUNDS BETWEEN 2 AND 50 K

Abstract

The specific heats of the intermetallic rare earth compounds LaNi$_5$, GdNi$_5$ and TbNi$_5$ have been investigated in the temperature range 2 to 50K in order to reexamine the low temperature specific heat of the non-magnetic LaNi$_5$ compound and to study the magnetic contributions to the specific heat in the magnetic GdNi$_5$ and TbNi$_5$ compounds around their Curie temperatures. The low temperature specific heat of the LaNi$_5$ compound shows an unusual anomaly.

The magnetic specific heats of the GdNi$_5$ and TbNi$_5$ compounds show λ-type anomalies. These compounds show other anomalies at about 3.8 K and 2.4 K respectively. These anomalies have been attributed to the presence of Gd$_2$O$_3$ and Tb$_2$O$_3$ magnetic compounds as impurities.

Keywords: *Specific Heat, Heat Capacity, Rear Earth Compounds, RE-Ni$_5$ Compounds, Magnetic Phase Transition.*

Résumé

La chaleur spécifique des composés intermétalliques de terre rare, LaNi$_5$, GdNi$_5$ et TbNi$_5$ ont été étudiés dans une gamme de température entre 2 et 50K, dans le but de réexaminer la chaleur spécifique à basse température du composé amagnétique LaNi$_5$ et d'étudier les contributions magnétiques de la chaleur spécifique dans les composés magnétiques GdNi$_5$ et TbNi$_5$ autour de leur température de Curie. La chaleur spécifique à basse température du composé LaNi$_5$ montre une anomalie.

La chaleur spécifique magnétique des composés GdNi$_5$ et TbNi$_5$ montre des anomalies de type λ. Ces composés montrent d'autres anomalies à environ 3.8K et 2.4K respectivement. Ces anomalies ont été attribuées à la présence des composés magnétiques de Gd$_2$O$_3$ et Tb$_2$O$_3$ comme impuretés.

Mots clés: *Chaleur spécifique, Capacité thermique, Composés de terre rare, Composés RE-Ni$_5$, Transition de phase magnétique.*

K.A. MOHAMED
Department of Physics
College of Education
University of Mosul
Mosul, Iraq

ملخص

تم في هذا البحث دراسة الحرارة النوعية لمركبات العناصر الأرضية النادرة مع عنصر النيكل LaNi$_5$ و GdNi$_5$ و TbNi$_5$ في مدى درجات الحرارة 2 إلى 50 درجة كلفنية. أظهرت الحرارة النوعية للمركب LaNi$_5$ تصرف غير طبيعيا في درجات الحرارة الأقل من 7K. كذلك أظهرت المساهمة المغناطيسية في الحرارة النوعية في المركبات GdNi$_5$ و TbNi$_5$ ذروات حادة عند درجة حرارة التحول في الطور المغناطيسي والمساوية إلى K 32 و 21 على التوالي. كما أظهرت هذه المركبات قيما صغيرة عند درجات الحرارة 3.8K و 2.4K سببها التحول في الطور المغناطيسي لذرات مركبات Gd$_2$O$_3$ و Tb$_2$O$_3$ التي تتواجد كشوائب في المركبات المغناطيسي GdNi$_5$ و TbNi$_5$.

الكلمات المفتاحية: *الحرارة النوعية، المركبات العناصر الأرضية النادرة، حرارة دييائي.*

The intermetallic RE-Ni5 (RE=rare earth metal) compounds crystallize in the hexagonal CaC$_5$ type structure [1]. These compounds (except PrNi$_5$) order ferro- or antiferro- magnetically at low temperatures. The PrNi$_5$ is known to be paramagnetic from specific heat and magnetic susceptibility measurements [2] the RE-Ni$_5$ compounds are isostructural with RE-Co$_5$ compounds, which are of great technological interest. Moreover, magnetic moments are observed at the Co sites while no moments have been reported at the Ni sites. It appear that the 3d shell of the Ni ions in all RE-Ni$_5$ compounds are filled by the valence electrons of the rare earth ions, accordingly the magnetic order in these compounds is due to the ordering of the rare earth moments [3].

Studies of the magnetic properties of the RE-Ni$_5$ compounds have been a subject of great interest. This is mainly due to prospects for using LaNi$_5$ compound in storage and purification of hydrogen technology and due to the successful application of PrNi$_5$ compound as a working medium for attaining ultra low temperatures by the nuclear demagnetization method [4-5].

The magnetic properties (except for GdNi$_5$) of these compounds are governed by the existence of the crystalline electric field (CEF) effects. The crystal field effects in the polycrystalline TbNi$_5$ and ErNi$_5$ compounds have been investigated on the basis of the inelastic neutron scattering experiments. In this study, the magnetic contributions to the

specific heat have been predicated and compared with low temperature specific heat results for single crystal [6]. Crystal field studies have also been reported for SmNi$_5$ [7] and PrNi$_5$ [8] compounds. The Gd is an S-state ion and the CEF-effects is very small (i.e. negligible). But measurements on single crystal sample of GdNi$_5$ showed the existence of d-band negative polarization at low temperatures [9].

Specific heat studies of theses compounds are quite rare. Specific heat measurements of LaNi$_5$, CeNi$_5$, PrNi$_5$ and GdNi$_5$ compounds have been reported in the temperature range 1.6 K to 4 K [10]. Specific heat measurements have also been reported for PrNi$_5$, LaNi$_5$ [2], TbNi$_5$ [11] and ErNi$_5$ [12] compounds for wider range of temperature.

Susceptibility, specific heat, magnetostriction and magnetoresistance measurements on polycrystalline TbNi$_2$ compound showed an additional magnetic phase transition at 14 K below the Curie temperature of T_C = 36 K. The additional phase transition has been attributed to the rotation of the Tb moments on some of the non-equivalent Tb sites in the unit cell [13].

The electronic specific heat coefficient and magnetic entropy of the Mg-RE-Zn (RE=Gd, Tb and Y) have been investigated. The specific heat of the Mg$_{42}$Gd$_8$Zn$_{50}$ exhibits a broad maximum at a temperature that a few Kelvins above the spin freezing temperature determined by AC susceptibility measurements. The magnetic specific heat of the Mg$_{42}$Gd$_8$Zn$_{50}$ is smaller than that of Mg$_{42}$Tb$_8$Zn$_{50}$ suggest the splitting of the ground state due to the local electrostatic field [14].

The specific heat of the pseudobinary TbNi$_{5-x}$Cu$_x$ and TbNi$_{5-x}$Al$_x$ alloys have been studied for certain values of x. The dependence of the Curie temperatures in these systems on x have been investigated. The substitution of Cu and Al for Ni decreases sharply the spontaneous magnetic moment, increases the magnetic anisotropy in the easy basal plane and leads to strong magnetic domain wall pinning. These results have been explained by the effects of random local crystal fields, band magnetism and heterogeneous polarization of the mixed 3d band [15].

The aim of this paper is to report measurements on the low temperature specific heat of the LaNi$_5$, GdNi$_5$ and TbNi$_5$ compounds in the temperature range 2 to 50 K in order to reinvestigate the low temperature specific heat of LaNi$_5$ compound and to estimate the magnetic entropy changes and magnetic contributions to the specific heat in the GdNi$_5$ and TbNi$_5$ compounds.

EXPERIMENTAL

The polycrystalline LaNi$_5$, GdNi$_5$, and TbNi$_5$ and samples were obtained by arc melting together (under reduced high purity argon atmosphere) the appropriate quantities of La, Gd, Tb and Ni of 99,99% nominal purity. Each alloy was turned and remelted at least four time to promote homogeneity. The loss in the total mass after alloying was less than 0.1% and this has been taken as justification for assuming that the proportion of elements in the final compound was the same as that of the starting mixture. The sample holder consists of a thin copper disc with an axial tube, which accommodates a small calibrated Lake Shore Type GR-200B germanium thermometer. The total mass of the sample holder was about 1g. The main button was cut into few pieces to be well distributed on a disc like copper samples holder. The small pieces were attached to the sample holder using several milligrams of diluted G.E.6031 varnish solution. The sample total mass was 4 to 7 g. The heat capacity was measured using a modified adiabatic continues heating technique from 4.2 K to 50 K while the heat pulse technique has been used in the temperature range 1.5 K to 7 K. The accuracy of the measured temperature and the heat capacity were better than +3 mK and 1% respectively. Details of the experimental apparatus and measurements techniques can be found in ref. [16].

RESULTS AND DISCUSSION

The total specific heat results, C$_p$, of the polycrystalline magnetic GdNi$_5$ and TbNi$_5$ compounds as function of temperature, T, are shown in figures 1 and 2 respectively. These figures also show the specific heat of the non-
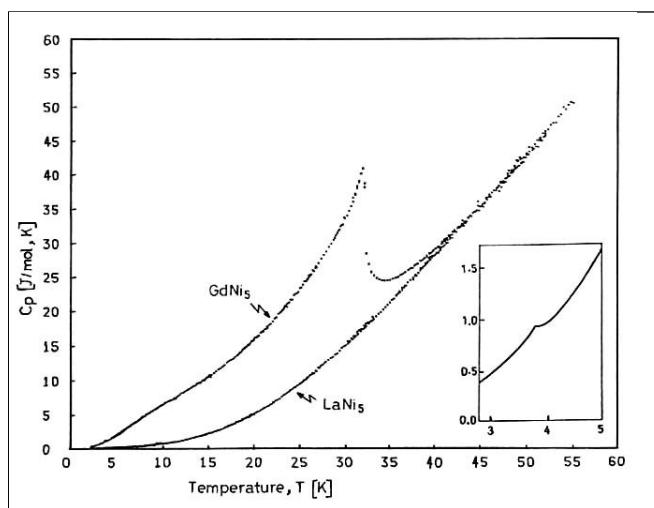

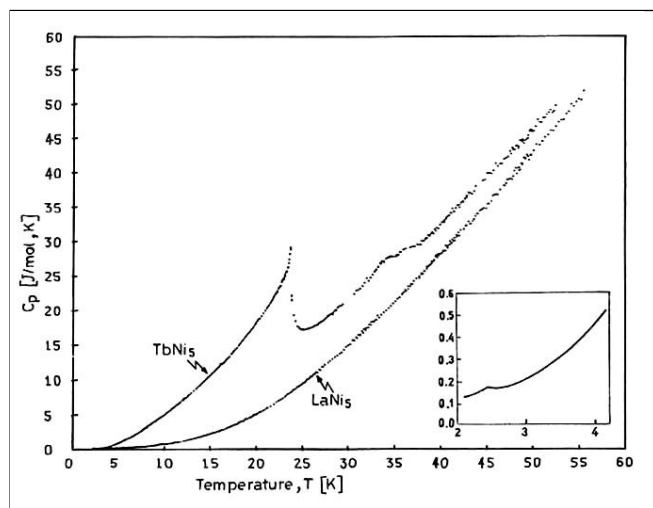**Figure 1:** The specific heat, C$_p$, versus temperature, T for LaNi$_5$ and GdNi$_5$ compounds.

Figure 2: The specific heat, C$_p$, versus temperature, T for LaNi$_5$ and TbNi$_5$ compounds.

magnetic LaNi$_5$ compound for comparison. Clearly, the GdNi$_5$ and TbNi$_5$ compounds exhibit excessive heats due to the magnetic effects. Moreover, the specific heat results of the magnetic compounds show λ-type anomalies at their Curie temperatures, which are characteristics of the cooperative phenomena. The maximum values of C$_p$ lie at a temperature, T$_m$ = 32K and 23.7K for GdNi$_5$ and TbNi$_5$ compounds respectively. Values of T$_m$ can be compared with Curie temperatures, T$_C$ of 36K for GdNi$_5$ compound and 27K [17] and 23K [18] for TbNi$_5$ compound determined by magnetization.

The specific heat of the GdNi$_5$ and TbNi$_5$ compounds show other anomalies at about 3.8K and 2.4K respectively (see the insets in figures 1 and 2). These anomalies have been attributed to the presence of Gd$_2$O$_3$ and Tb$_2$O$_3$ magnetic impurities. The Gd$_2$O$_3$ and Tb$_2$O$_3$ compounds undergo antiferromagnetic phase transition at their Neel temperature, T$_N$ of 3.7K and 2.4K respectively [19]. Similar anomalies have been exhibited by many Gd- and Tb- compunds such as pure Gd- and Tb- metals [20-21], GdAg [22-23] and TbAg [24] compounds at approximately the same temperatures. These anomalies have been attributed to the presence of Gd$_2$O$_3$ and Tb$_2$O$_3$ magnetic impurities.

The total specific heat, C$_p$, of the magnetic compound can be expressed by the equation C$_p$=C$_e$+C$_l$+C$_m$ where C$_e$, C$_l$ and C$_m$ are the electronic, lattice and magnetic contributions to the specific heat respectively. The C$_e$ and C$_l$ terms represent the non-magnetic contribution to the specific heat at low temperature in the RE-Ni$_5$ compounds can be approximately represented by the specific heat of the non-magnetic LaNi$_5$ compound [25-29].

Results of the specific heat of the LaNi$_5$ compound are in very good agreement with reported results [30] for temperature higher than 20K. But results of this study are higher than those reported previously for temperatures less than 20K and the difference between the two results increases up to 15% as temperature decreases to 10K. The low temperature end of LaNi$_5$ results are reshown in figure 3 as C$_p$/T versus T^2 in the temperature range 2 to 10K. These results are in good agreement with reported results [10]; they overlap in the concerned range of temperatures. In fact, the clear anomaly in C$_p$ of LaNi$_5$ at low temperatures could not be seen by ref. [10] because the temperature range of those measurements extends up to 4K only, while the temperature range of this anomaly extends up to 7K. This lead to the analysis of the low temperature results by assuming only the electronic and lattice terms [10]. Clearly, this assumption might not be true. Indeed, the present results show an extra and unusual anomaly. This anomaly might be caused by a residual clustering of Ni atoms, which leads to a degree of a super-paramagnetism. This point can be clarified further by a systematic study of the magnetization of the LaNi$_5$ compound as a function of temperature and field, which will give quantitative information on both the size and concentration of the Ni clusters. The presence of such term makes any assumption of the electronic and the lattice specific heat coefficients quite difficult and liable to produce significant errors. Therefore, the specific heat data in the temperature range 7 to 10K have been employed to estimate the electronic, γ,

and lattice, β, specific heat coefficients. The data in this range of temperature can be represented by the expression; C$_p$ = 10T+0.61T^3 where C$_p$ is in mJ/mol,K units. A constant values of about 10 mJ/mol,K^2 was widely accepted as a reasonable representative of this coefficient for many rare earth alloys [20-21]. The coefficient of the cubic term leads to a Debye temperature of θ$_D$(0) =147±2K, which agrees quite well with values reported for La-compounds at low temperatures [20]. The new values of γ and θ$_D$(0) are substantially disagree with previously reported results [10], in which values of γ and θ$_D$(0) are found equal to 34.33mJ/mol,K^2 and 341K respectively.
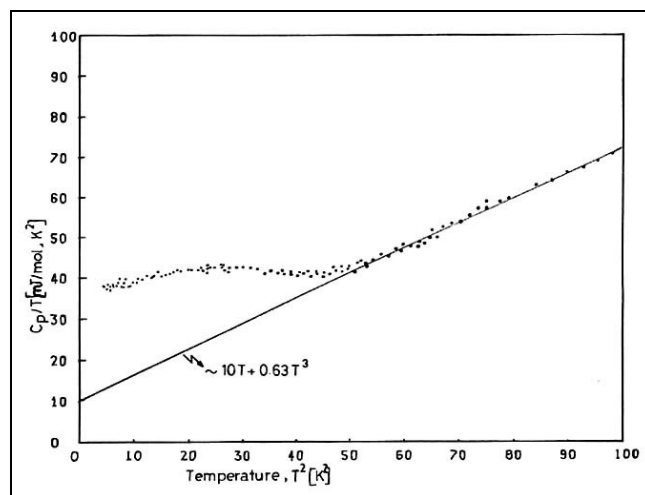

Figure 3: C$_p$/T versus T^2 for LaNi$_5$ compound.

The specific heat of the anomaly, Cex has been obtained by the subtraction of the normal behaviors (=10T+0.61T^3) from the total specific heat of LaNi$_5$ compound at low temperatures. Values of Cex have been plotted in figure 4 as Cex versus T^2. Clearly, this anomaly shows a broad anomaly centered at about 4.5K and the high temperature tail of this anomaly goes approximately as Cex~1/T^2, such behaviors are in favor of Ni atoms clustering idea [31].

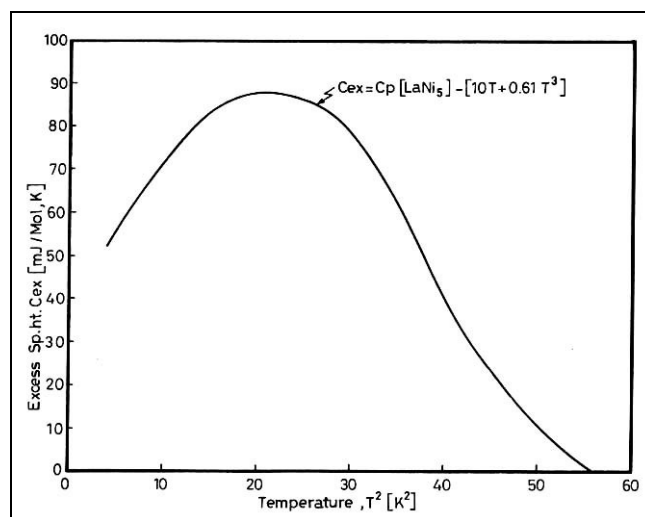**Figure 4:** Excess specific heat, Cex versus T^2 for LaNi$_5$ compound.

Figure 5: The magnetic specific heat, C_m, versus T for GdNi$_5$ compound.
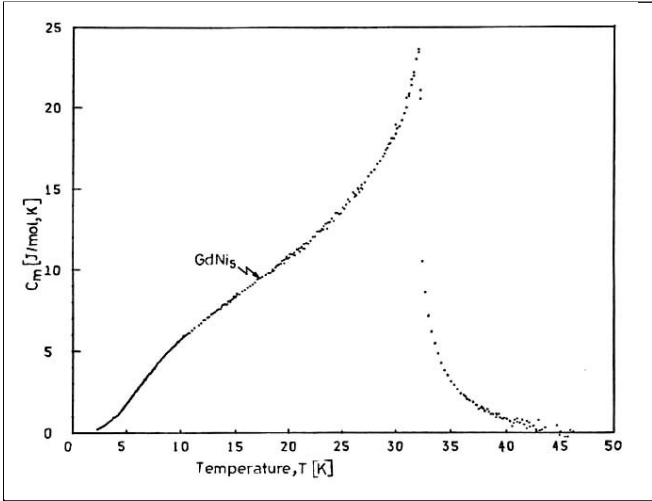

Figure 6: The magnetic specific heat, C_m, versus T for TbNi$_5$ compound.

As it has been mentioned earlier that the specific heat of non-magnetic LaNi$_5$ compound has been considered to represent the non-magnetic contributions to the specific heat in the magnetic RE-Ni$_5$ compounds. Therefore, the magnetic contributions to the specific heat, C_m, of the GdNi$_5$ and TbNi$_5$ compounds have been obtained by simply subtracting the total heat of LaNi$_5$ compound from their total specific heats. The results of these subtractions have been plotted in figures 5 and 6 as C_m versus T over the entire range of measurement for GdNi$_5$ and TbNi$_5$ respectively. C_m exhibits a very clear λ-type anomaly whose maximum cited at a temperature, T_m, of 32K and 23.7K for GdNi$_5$ and TbNi$_5$ compounds respectively. The specific heat of the GdNi$_5$ compound shows another anomaly at about 3.8K as shown in figure 1. This maximum has been attributed to the presence of the magnetic impurities of the Gd$_2$O$_3$ compounds. Similar behaviors have been reported at 3.7K [19].The value of the peak in C_p at 3.8K is higher than the reported peak in Cp at 3.8K is higher than the reported peak value at 3.6K [10] by about 50%. Moreover, C_m exhibits a shoulder in the temperature range between 5 and 20K. The presence of the maximum in C_m at low temperatures makes the search for any spin wave contributions to the magnetic specific heat quite difficult. The magnetic specific heat of the TbNi$_5$ compound agrees quite well with those calculated theoretically [6] and experimentally [11]. This differences reach to about 10% as temperature rises to T_m. C_m has its maximum value, C_m(max)(=21J/mol, K) at T_m=23.7 K. Values of C_m(max) and T_m can be compared with reported experimental results (=18.8 J/mol, K) at 21.5K [11] and theoretically calculated results (=18.5 J/mol, K) at 22.3 K [6], which were based on crystal field effects. The low temperature end of C_m of the TbNi$_5$ compound shows another anomaly at about 2.4K as shown in figure 2. This maximum has been attributed to the presence of magnetic impurities of the Tb$_2$O$_3$ compound, which shows an antiferromagnetic transition at 2.4K [16].

The magnetic entropy changes S_m are related to the magnetic specific heat by the relation : $S_m = \int (C_m/T)dt$.
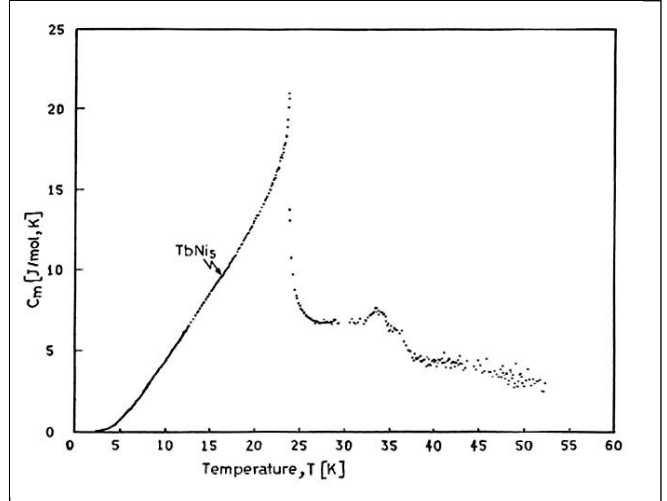
Accordingly, the magnetic entropy changes between T=0K and T=T_m, (where T_m represents the temperature at which C_m has its maximum) have been obtained by the integration of the smoothed magnetic specific heats between T=0K and T_m=32K and 23.7K for GdNi$_5$ and TbNi5 compounds respectively, where the low temperature C_m results have been smoothly extrapolated to 0 value at T=0K. The estimated values of S_m are 16.4±0.1 and 10.4±0.1 J/mol,K for GdNi$_5$ and TbNi$_5$ compounds respectively. These values are equal to about 95% and 49% of the molar magnetic entropy, S_m(max)=R.Ln(2J+1) where R is the gas constant and J is the spin of the magnetic element which equals to 7/2 and 6 for Gd and Tb ions respectively. These values confirm the fact that there are still significant excessive magnetic heat capacities associated with short range magnetic ordering above the Curie temperature for the TbNi$_5$ compound. The main part of the magnetic contributions to the specific heat at temperature higher than Curie temperature have been attributed to the crystalline electric field interactions of the low lying energy levels of the Tb ions producing a Schottky-like anomaly with broad maximum centered at about 34K. Values of the specific heat parameters determined by this study and others are summarized in table 1.

Sample Composition	T_C or T_N (K)	Results of other refs.	S_m/R.Ln(2J+1) (%)	S_m 0→T_m (J/mol,K)
LaNi$_5$	Non-magnetic	-------	-------	--------
GdNi$_5$	32	36[17]	95	16.4
TbNi$_5$	23.7	27[17] 23[18]	49	10.6
Gd$_2$O$_3$	3.8	3.7[19] 3.6[10]	-------	-------
Tb$_2$O$_3$	2.4	2.4[19]	-------	-------

Table 1: Values of T_C(T_N), S_m and S_m(max).

CONCLUSION

Specific heat measurements for rare earth polycrystalline samples LaNi$_5$, GdNi$_5$ and TbNi$_5$ compounds have been presented in the temperature range 2 to 50K. The low temperature specific heat results of the LaNi$_5$ compound exhibit an extra and unusual anomaly, which has been attributed to the Ni clusters leading to a kind of super-paramagnetism; magnetization investigation is needed for its confirmation. Values of the electronic and lattice heat coefficients of the LaNi$_5$ compound are in disagreement with those reported previously. The two anomalies in the specific heats of both GdNi$_5$ and TbNi$_5$ compounds result from the presence of the Gd$_2$O$_3$ and Tb$_2$O$_3$ magnetic impurities and the phase transition from the ferromagnetism to paramagnetic states at their Curie temperatures. The estimated values of the magnetic entropy changes between 0K and Curie temperatures do not exceed the expected maximum magnetic entropy values, R.Ln(2J+1) for Gd and Tb ions in the GdNi$_5$ and TbNi$_5$ compounds

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