Magnetic and thermodynamic properties of GdCu₄Au

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Abstract. The results of magnetic susceptibility, \(\chi(T)\), magnetization, \(\sigma(\mu_0 H)\), and specific heat, \(C_P(T)\), for GdCu₄Au are presented. The room temperature powder X-ray diffraction studies indicate a cubic MgCu₄Sn - type crystal structure with space group \(F\bar{4}3m\) (No.216). The low field dc \(\chi(T)\) data shows an antiferromagnetic - like (AFM) anomaly associated with a Néel temperature \(T_N = 10.8\) K for GdCu₄Au. In the paramagnetic region above \(T_N\), \(\chi(T)\) data follows the Curie - Weiss law with an effective magnetic moment \(\mu_{eff} = 7.444(1)\) \(\mu_B\) and paramagnetic Weiss temperature \(\theta_P = -15.01(2)\) K. The experimental value of \(\mu_{eff}\) is close to the calculated value of 7.94 \(\mu_B\) expected for the free Gd\(^{3+}\)-ion. The field-cooled (FC) and zero-field-cooled (ZFC) \(\chi(T)\) data provide evidence for the formation of spin-glass state with a freezing temperature \(T_f = 15\) K. \(\sigma(\mu_0 H)\) measured in the ordering region (below \(T_N\)) shows that GdCu₄Au undergoes metamagnetic transition above 0.7 T, characterized by a slight upward curvature above this field. Measurement of \(\sigma(\mu_0 H)\) in the paramagnetic regions show a linear behaviour up to 0.7 T and a downward curvature at high fields. \(C_P(T)\) data shows an AFM - like phase transition at \(T_N = 10.4\) K close to the phase transition observed in \(\chi(T)\) results. The 4f-electron entropy reaches the value of \(R\ln 2\) close to \(T_N\) at 9.02 K and reaches the value of \(R\ln(2J+1)\) at \(T = 180\) K.

1. Introduction
The studies of binary intermetallic compounds RECu₅ (RE = rare earth elements), indicate that these compounds exhibit an interesting crystallographic feature depending on the RE ion [1, 2]. The compounds with heavy RE elements (RE = Ho, Er, Tm) have the cubic AuBe₅ - type structure. For light RE elements (RE = La - Sm) and incidentally also for some heavy RE elements, a hexagonal compound of the CaCu₅ - type has been reported in the literature [3, 4, 5]. For those compounds with RE elements in the intermediate region (RE = Gd, Tb, Dy) or Y, the crystallographic structure would be the cubic or the hexagonal one depending on the heat treatment given to the samples [6, 7]. Several investigations were devoted to the substitution of one Cu with M atoms, RECu₄M, (M = Ag, Au, Pd, Al, In) on the crystallographic, magnetic and electrical properties and these lead to phases crystallizing in the cubic MgCu₄Sn prototype (a ternary variant of AuBe₅) [8, 9, 10, 11, 12, 13, 14, 15]. For instance, RECu₄Au and RECu₄Pd
are isostuctural with RECuAg which adopts the cubic MgCu4Sn - type structure and the Au or Pd are situated at the (1/4, 1/4, 1/4) positions of the unit cell. Aside from the crystallographic structure, the transport and magnetic properties of these compounds RECuM were found to display interesting features, particularly those which crystallize in the hexagonal CaCu5 - type structure [16, 17, 18, 19]. For instance semi - metallic - like behaviour was observed in YCu4In and GdCu4In analogues and exchange frustrated antiferromagnetism (AF) in GdCu4In [20, 21, 22]. While GdCu5 orders AFM at 12.5 K [7], GdCu4Pd orders ferromagnetically (FM) with a Curie temperature $T_C = 110$ K [6], which means, the replacement of one Cu atom with Pd atom considerably affects the conduction electron - mediated RKKY exchange interaction in GdCu5, similar in TbCu5 with the substitution of Cu atom with Pd [23]. Ferromagnetic ordering was also observed in other compounds with light RE elements such as PrCu4Pd ($T_C = 5$ K), NdCu4Pd ($T_C = 12$ K), SmCu4Pd ($T_C = 28$ K) and EuCu4Pd ($T_C = 24.5$ K) [6]. The first - order valence transition in YbCu4M has been reported in the literature as well as the studies of YbCu4M (M = In, Ni, Pd, Cd, Mg, Ti, Au and Ag) [24, 25]. A complex inhomogeneous magnetic state arising from Cu - Mn disorder, 3d−3d and 3d−4f interaction has been reported in RECu4Mn compounds (RE = La - Sm, Gd) which have the hexagonal crystal symmetry of the parent compound RECu5 [27].

The studies of the magnetic structure of GdCu5 in particular have been reported in the literature. Neutron diffraction experiments at very short wavelength where the absorption cross section of Gd is not too high, indicates that below $T_N$, GdCu5 orders in an incommensurate triangular structure associated with a propagation vector $Q = 1/3, 1/3, 0, 0.223$ [19]. This incommensurate magnetic structure arises from the weak negative interaction between Gd nearest neighbours. Furthermore, the usual magnetic properties and the behaviour of low temperature resistivity seem to be related to the incommensurate magnetic structure in compounds without magnetocrystalline anisotropy [19].

In view of these peculiar magnetic properties of GdCu5 compound, it would be interesting to investigate the effect of substituting one Cu atom with Au atom in magnetic and thermodynamic properties of GdCu4Au.

2. Experimental procedures

The polycrystalline samples of GdCu4Au and LuCu4Au were prepared by arc-melting stoichiometric amounts of the constituent elements on a water - cooled copper plate in an arc - furnace. Metals of the following purity in wt% were used: Gd, Lu and Au: 99.99; Cu: 99.995. Melting was performed in a titanium gettered ultra - high purity argon atmosphere and ingots were turned over and remelted several times to ensure good homogeneity. Losses in weight after melting were smaller than 1%. Samples thus prepared were characterized by X - ray powder diffraction using a Bruker D8 Advance diffractometer with a CuKα radiation ($\lambda = 1.540598$ Å). The diffraction patterns were analyzed using the Rietveld and CAILS - Pawley (cell and intensity least - squares) method.

Temperature - and magnetic field- dependent properties of the prepared compounds were measured using a Physical Property Measurement System (PPMS; Quantum Design). The magnetic susceptibility and magnetization were measured using the Vibrating Sample Magnetometer (VMS also Quantum Design).

3. Results and discussion

3.1. Crystallographic

X - ray diffraction spectra showed that the two compounds are single phase as their diffraction peaks could be indexed to appropriate crystal symmetries, although for LuCu4Au there remains a weak impurity peak (the intensity is at most less than 8.6% of the most intense major - phase peak) as indicated by the arrow in figure 1. X-ray diffractograms obtained for GdCu4Au and
LuCu$_4$Au compounds together with full-profile least-squares (LSQ) refinement fits to the data are shown in figure 1. The space group setting used in the refinement was $F\overline{4}3m$ of the cubic MgCu$_4$Sn-type structure. The resulting cubic crystal structure is depicted in figure 2 and the atomic coordinates in GdCu$_4$Au are listed in table 1. The refined room-temperature lattice parameters and the unit cell volume values are: $a = 7.143(3)$ Å and $V = 364.5(5)$ Å$^3$ for GdCu$_4$Au and $a = 7.051(2)$ Å and $V = 350.5(3)$ Å$^3$ for LuCu$_4$Au. The bigger value of $V$ for the Gd compound compared to the Lu compound is a consequence of the bigger atomic radius for Gd than for Lu.

![Figure 1](image1.png)

Figure 1. (Color online) Rietveld analyzed diffraction patterns for GdCu$_4$Au and LuCu$_4$Au. The observed data are shown by green symbols and the solid red lines through the data represent the results of the structure Rietveld refinement. The lower black curves are the difference curve for the experimental data and the calculated curve. The arrow indicates unreacted element.

![Figure 2](image2.png)

Figure 2. (Color online) The cubic crystal structure of RECu$_4$Au (RE = Gd or Lu). The black spheres represent the RE atom, the red spheres represent the Cu atom and the yellow spheres represent the Au atom.

**Table 1.** Atomic coordinates for GdCu$_4$Au obtained from the full-structure Rietveld refinement method using the $F\overline{4}3m$ space group. The site occupancies of the atoms was kept fixed at 100%.

| Atoms | Wyckoff site | $x$     | $y$     | $z$  |
|-------|--------------|---------|---------|------|
| Gd    | 4a           | 0       | 0       | 0    |
| Cu    | 16e          | 0.6258(1)| 0.6258(1)| 0.6258(1) |
| Au    | 4c           | 1/4     | 1/4     | 1/4 |

3.2. Magnetic susceptibility and magnetization

The temperature dependence of the inverse magnetic susceptibility, $\chi^{-1}(T)$ measured in applied field of 0.01T in the temperature range 2 - 300 K are depicted in figure 3 for GdCu$_4$Au compound.
Figure 3. (color online) $\chi^{-1}(T)$ for the GdCu$_4$Au. The solid red lines are LSQ fits of Eq.1 to the measured data above $T_N$.

Figure 4. Low temperature $\chi(T)$ data measured in zero - field cooled (ZFC) and in field - cooled (FC) run. The arrows indicate the magnetic phase transition temperature $T_N$ and the freezing temperature $T_f$. The inset shows the field dependence of the magnetization measured at 2 K and 15 K in field up to 7 T.

It is observed that $\chi^{-1}(T)$ data obey the Curie - Weiss (CW) magnetic behaviour of GdCu$_4$Au above $T_N$, leading to an effective magnetic moment $\mu_{\text{eff}} = 7.444(1)$ $\mu_B$ and a paramagnetic Weiss temperature $\theta_p = -15.01(2)$ K when fitted to the CW law:

$$\chi^{-1}(T) = \frac{3k_B(T - \theta_p)}{N_A\mu_{\text{eff}}^2}.$$  \hfill (1)

The obtained $\mu_{\text{eff}}$ value is close to the free - ion Gd$^{3+}$ Hund’s rule expectation value, $g_J[J(J+1)]^{1/2} = 7.94 \mu_B$. Deviation of the CW behaviour below $T_N$ may be attributed to magnetic ordering or crystal - electric field effect. To further explore the low temperature magnetic state of GdCu$_4$Au, the low temperature field - cooled (FC) and zero - field - cooled $\chi(T)$ data are depicted in figure 4. Both FC and ZFC $\chi(T)$ data rises into an anomaly at $T_N = 10.8$ K which is attributed to a putative AFM - like phase transition for this compound. Furthermore, it is observed that the FC and ZFC $\chi(T)$ data split into two branches above $T_N$ at a freezing temperature $T_f = 15$ K. Such a bifurcation may originate from an inhomogeneous magnetic ground state in this compound, as a result a spin - glass - like state may form that causes the bifurcation or from an accidental magnetic history of the sample. It should be noted that the observed thermomagnetic irreversibility of GdCu$_4$Au is very small compared to other RE compounds such as RENi$_4$Si [29]. It was pointed out that the large thermomagnetic irreversibility observed in RENi$_4$Si arise from the anisotropy due to RE - ion except for the Gd compound. However, the small thermomagnetic anisotropy for the Gd compound is due to the fact that Gd - ion is characterized by the orbital momentum $L = 0$ implying a negligible magnetic anisotropy also observed in our sample. Our value of $T_N = 10.8$ K obtained for GdCu$_4$Au may be compared to the values of $T_N = 10$ K and 12.5 K reported in the literature for the parent compound GdCu$_5$ [28, 7]. This similarity of $T_N$ values of GdCu$_4$Au and GdCu$_5$,
suggest that conduction electron-mediated RKKY exchange interaction in \( \text{GdCu}_5 \) is not affected by substitution of \( \text{Au} \) for \( \text{Cu} \) in contrast for \( \text{TbCu}_5 \) compound with the substitution of \( \text{Pd} \) for \( \text{Cu} \) [23].

**Figure 5.** The specific heat \( C_p(T) \) of \( \text{GdCu}_4\text{Au} \) (opened circle) and \( \text{LuCu}_4\text{Au} \) (opened triangle). The inset shows the low temperature \( C_p(T) \) with the arrow at the magnetic phase transition.

\( \sigma(\mu_0H) \) measured below and above \( T_N \) (2 K and 15 K) in field up to 7 T are depicted in the inset of figure 4. It is observed that \( \sigma(\mu_0H) \) measured below \( T_N \) at 2 K and above \( T_N \) at 15 K, increase linearly with field up to 0.7 T, and exhibits a slight upward curvature above this field which may be attributed to metamagnetic transition for \( T = 2 \text{K} \) and a downward curvature for \( T = 15 \text{K} \).

3.3. *Specific heat*

The temperature dependence of specific heat \( C_p(T) \) of \( \text{GdCu}_4\text{Au} \) and the nonmagnetic reference compound \( \text{LuCu}_4\text{Au} \) are displayed in figure 5. For the isomorphous nonmagnetic reference compound, \( C_p(T) \) varies monotonically with no anomaly down to 1.8 K, while in \( C_p(T) \) of \( \text{GdCu}_4\text{Au} \), a sharp peak is observed at the magnetic phase transition temperature \( T_N = 10.4 \text{K} \) (inset of figure 5). This value is close to that observed in the susceptibility data. At higher temperature, \( C_p(T) \) curve reach the classical value of \( 3NR = 149.7 \text{J/K} \) of the Dulong-Petit law around 180 K and 250 K for \( \text{GdCu}_4\text{Au} \) and \( \text{LuCu}_4\text{Au} \) respectively (dotted line in figure 5) due to the vibrational mode of \( N = 6 \) atoms per formula unit. No evidence of charge or spin-density wave was observed on the \( C_p \) data of \( \text{GdCu}_4\text{Au} \) compound below \( T_N \). The magnetic contribution to the specific heat \( C_{4f}(T) \) as well as the magnetic entropy \( S_{4f}(T) \) are shown in figure 6. \( C_{4f}(T) \) calculated by subtracting the \( C_p(T) \) of \( \text{LuCu}_4\text{Au} \) from that of \( \text{GdCu}_4\text{Au} \). The maximum observed in \( C_{4f}(T) \) curve, may originate from the large difference in the lattice vibrational spectra of the two compounds as a consequence of the bigger atomic mass for \( \text{Lu} \).
than for Gd. It could also originate for the fact that Gd ion is characterized by a total angular momentum $L = 0$ with $J = S$. It should be noted that, the impurity observed in the non-magnetic counterpart may have an impact on the specific heat measurements, leading to a considerable uncertainty in the estimation of $C_{4f}$. Therefore, we cannot attribute the observed maximum at high temperature to a Schottky anomaly being a result of crystal - electric field splitting of the ground state level. The magnetic entropy $S_{4f}$ was calculated from the magnetic part $C_{4f}(T)$ of GdCu$_4$Au: $S_{4f}(T) = \int_0^T [C_{4f}(T')/T']dT'$. At $T_N$, $S_{4f}(T)$ reaches nearly 24.5% more of the value of $R\ln(2)$ as expected for the two - level ground state and 15% more of the value of $R\ln(2J + 1) = R\ln(8)$ at room temperature.

3.4. Conclusions

XRD studies indicate the ordered cubic MgCu$_4$Sn - type structure with space group $F\bar{4}3m$ for GdCu$_4$Au and LuCu$_4$Au compounds. Magnetic susceptibility results indicate a putative AFM behaviour and a possible spin - glass behaviour. Magnetization data indicate metamagnetic behaviour above 0.7 T at a temperature below $T_N$. Specific heat result confirms that the phase transition, of putative AFM character also observed in the susceptibility data, has an associate anisotropy.

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