

Anomalous structural properties of some RCu_2Ge_2 compounds ($\text{R} = \text{La}, \text{Gd-Tm}$)

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In this paper, we address the issue of possible quadrupole ordering in RCu_2Ge_2 compounds. In the literature, there are reports on anomalous behaviour of lattice parameters, however, lack of high quality data makes the relevant analysis dubious. Therefore, we attempt to perform precise, non-ambient XRD measurements within 12 – 300 K temperature range. Our results confirm peculiar temperature behaviour of the c -lattice parameter that exhibits a well defined minimum at about 60 – 120 K for majority of investigated compounds. However, in contrast to the literature, the anomalous behaviour does not exhibit discontinuities. On the other hand, such behaviour has been evidenced for La-based compounds (LaCu_2Ge_2 and LaNi_2Ge_2), where the 4f orbitals are unoccupied.

Keywords: *rare-earth intermetallics; non-ambient X-ray diffraction*

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1. Introduction

The germanides of RCu_2Ge_2 stoichiometry are well known for their intriguing properties. The most prominent member of that family is the CeCu_2Ge_2 Kondo system, where antiferromagnetic ordering below approximately 4 K has been evidenced [1–4]. Moreover, the compound exhibits pressure-induced superconductivity [5, 6]. Other compounds of that family exhibit interesting magnetic properties at low temperatures [7–12]. Very intriguing strong electronic correlations were discovered in other isostructural compounds with 1:2:2 stoichiometry. Namely, the iron pnictides exhibit unusual superconductivity in proximity of antiferromagnetism [13]. It was found that the pairing mechanism is not related to electron-phonon but to spin fluctuation coupling [13].

The investigated family crystallizes within the body-centred tetragonal ThCr_2Si_2 structure (space group $I4/mmm$) with R, Cu, Ge atoms occupying 2(a), 4(d) and 4(e) positions respectively. A se-

quence of monoatomic layers (R–Cu–Ge–Cu–R) stacked along the c -axis is the key feature of the considered germanides. Especially, the values of the c/a ratio and Ge positional parameter are in a close relation to the observed magnetic structures [14]. For some members of the RCu_2Ge_2 family ($\text{R} = \text{Pr}, \text{Ce}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$ and Tm) temperature dependence of lattice parameters is known [15]. However, the available data are estimated with large errors (see Fig. 2 from [15]). The observed anomalies in temperature dependence of the c -lattice parameter are attributed to quadrupolar ordering of the 4f shell.

Our paper brings the very precise structural analysis of some polycrystalline RCu_2Ge_2 intermetallic compounds with $\text{R} = \text{La}, \text{Gd-Tm}$ at 12 – 300 K temperature range. In context of our data, the quadrupolar ordering scenario seems to be questionable.

2. Experimental

The investigated RCu_2Ge_2 ($\text{R} = \text{La}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$ and Tm) polycrystalline samples were synthesised by arc melting of stoichiometric

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amounts of high-purity elements (R of 99.9 % purity, Cu and Ge of 99.999 % purity) under argon atmosphere using Ti as a getter. In order to achieve good homogeneity of the samples, the melting procedure was repeated several times. Finally, the products were annealed in evacuated quartz tubes at 800 °C for two weeks. Preliminary phase analysis was done by X-ray powder diffraction (XRD) at room temperature using the PANalytical Empyrean diffractometer with CuK α radiation. All specimens were found to exhibit the expected structure. XRF measurements confirmed the required 1:2:2 composition of all investigated samples.

Low-temperature XRD measurements were done using Oxford Instruments Phoenix closed-cycle refrigerator. The Phoenix sample stage operated within 12 – 300 K temperature range. The position of the sample was corrected against temperature displacements during the measurements (tungsten powder of 99.9999% purity was used as a standard). Before each scan, the temperature was stabilized for 30 min. During the measurements the temperature deviation was less than 0.04 K. The data were analyzed using the Rietveld-type program FullProf [16]. For estimation of uncertainties (given in parentheses) the N_{SCOR} parameter was taken into account.

3. Results

3.1. LaCu₂Ge₂

The first investigated sample was LaCu₂Ge₂. At 300 K the refined lattice parameters are: $a = 4.21539(15)$ Å; $c = 10.17878(37)$ Å; $z_{Ge} = 0.3760(4)$; $V = 180.871(20)$ Å³ and $R_{Bragg} = 7.01$ %. The above values are close to those reported in the literature [17], however, our estimation of c is slightly higher. The temperature dependence of the above parameters is presented in Fig. 1. The a -parameter behaves typically, as can be deduced from the Fig. 1. At low temperatures it is nearly constant, up to roughly 30 K, then it rises with the temperature in a quasi-linear manner. Contrarily, the c -parameter exhibits a deep minimum at about 100 – 110 K (see Fig. 1). The further rise in temperature leads to an increase of c but the value

from 12 K is regained at 200 K and progresses constantly up to the value retrieved at 300 K.

The positional parameter of Ge is constant within the error bars in the entire temperature range. The unit cell volume shows no anomalies as it starts to increase above 50 K and continues this tendency up to 300 K (see Fig. 1). The reliability R_{Bragg} parameter is within a range of 6.87 – 7.01 %.

3.2. GdCu₂Ge₂

At 300 K the lattice parameter were found to be as follows: $a = 4.06414(15)$ Å; $c = 10.26015(38)$ Å; $z_{Ge} = 0.3780(4)$; $V = 169.469(20)$ Å³ and $R_{Bragg} = 6.75$ %. Remarkably, the c -parameter is higher than in case of La-based analogue, while the a is smaller. Accordingly to expected lowering of the radii of subsequent lanthanides, the unit cell volume is significantly decreased in comparison to the LaCu₂Ge₂. The above phenomena are in line with the previous findings [17]. The temperature variation of the a -parameter is shown in Fig. 1. The rise above 20 K is very similar to La-based sample. Although the c -parameter does not show such well-defined minima at low temperatures, its behaviour is still anomalous (Fig. 1). There is a shallow minimum at about 50 K, however, it is hardly above the uncertainty level. The z_{Ge} parameter slightly changes with the temperature. Above roughly 40 K, the unit cell volume increases in an expected manner (see Fig. 1). The highest value of the reliability R_{Bragg} parameter has been 6.83 %.

3.3. TbCu₂Ge₂

Thermal dependence of lattice parameters for TbCu₂Ge₂ is substantially different from that for Gd-based sample. The lattice parameters at 300 K are: $a = 4.04258(13)$ Å; $c = 10.28130(34)$ Å; $z_{Ge} = 0.3807(5)$; $V = 168.023(18)$ Å³ and $R_{Bragg} = 6.14$ % (the highest value among all temperatures). At low temperatures, the anomalous behaviour of c -parameter was evidenced with deep minimum at about 80 K. The second lattice parameter behaves in an expected way similarly to the unit cell volume (see Fig. 1), while the Ge positional parameter is constant within errors bars.

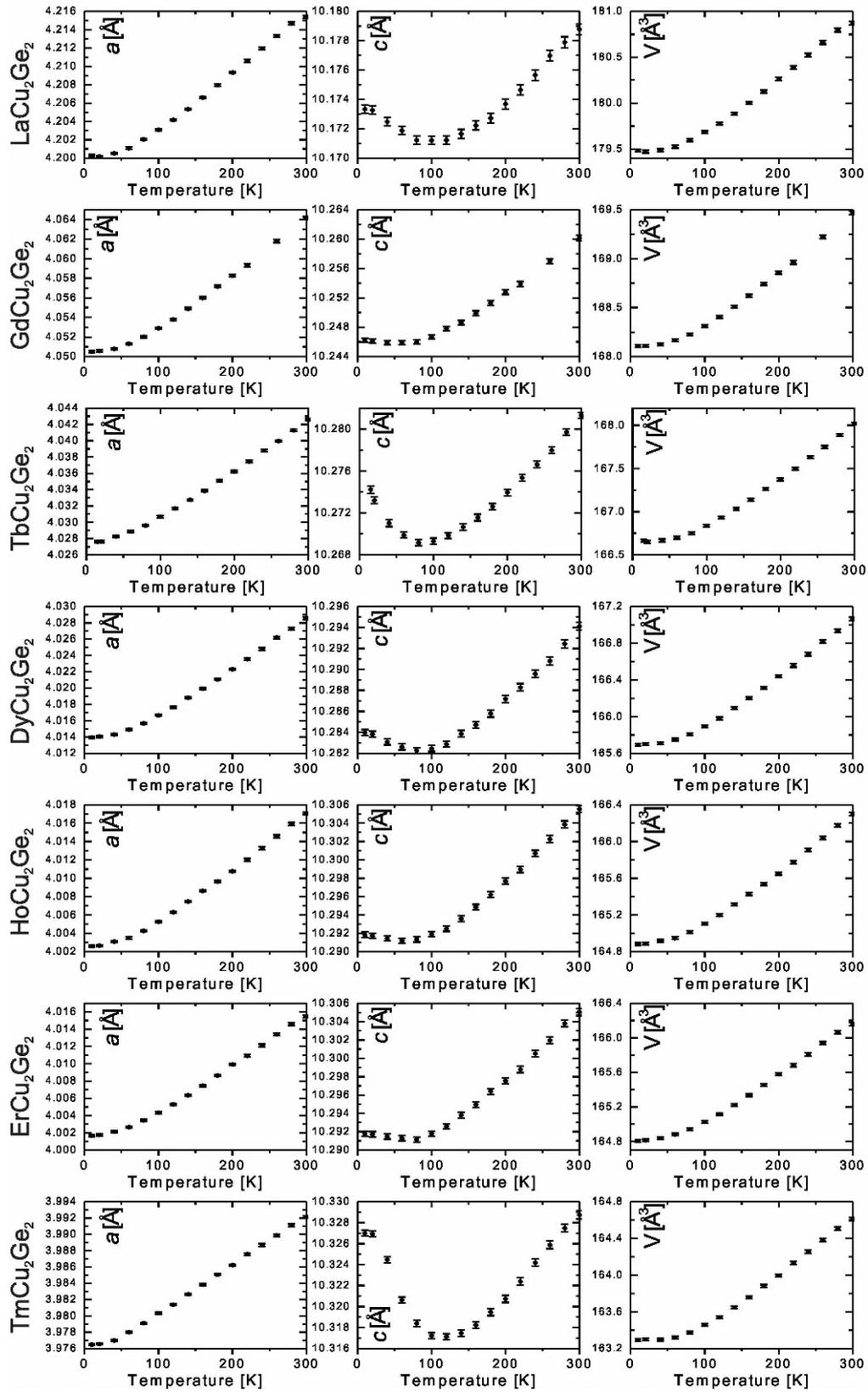


Fig. 1. Temperature dependence of the lattice parameters of RCu_2Ge_2 ($R = La, Gd-Tm$) compounds.

3.4. DyCu₂Ge₂

Measurement at 300 K revealed the following lattice parameters: $a = 4.02856(16)$ Å; $c = 10.29413(37)$ Å; $z_{Ge} = 0.3825(4)$; $V = 167.066(21)$ Å³ and $R_{Bragg} = 6.59$ %. The refined values are similar to those reported [17]. The volume consequently decreases in comparison to the predecessors, while the tendencies of both lattice parameters are still divergent. Similarly to the other investigated compounds, the a -parameter increases in the whole temperature range, while the c -parameter exhibits a minimum at 80 K (see Fig. 1). The positional Ge parameter is roughly constant. The unit cell volume exhibits plateau in between 12 – 50 K and starts to increase with the temperature in a quasi-linear manner (Fig. 1). The highest value of the reliability R_{Bragg} parameter has been 6.98 %.

3.5. HoCu₂Ge₂

The lattice parameters follow the tendency observed so far: $a = 4.01707(14)$ Å; $c = 10.30555(36)$ Å; $z_{Ge} = 0.3820(3)$; $V = 166.299(17)$ Å³ and $R_{Bragg} = 6.11$ % (which is the highest R_{Bragg} value calculated for this compound at any temperature). Those values are in agreement with the literature [17]. The discussion of temperature variation of the lattice parameters is entirely analogous to the previously discussed cases (see Fig. 1). It is worth noting that the minimal value of the c -parameter can be found in between 60 – 80 K, although the deepness of it is not as high as in the previous case. It seems that the unit cell volume starts to increase at lower temperature than that for the compounds discussed above.

3.6. ErCu₂Ge₂

For this compound, both lattice parameters are smaller than for the previous compound. Hence, a return to expected lanthanide contraction is observed (according to [15] such tendency should hold for YbCu₂Ge₂). Namely, the structural parameters at 300 K are: $a = 4.01549(15)$ Å; $c = 10.30504(37)$ Å; $z_{Ge} = 0.3819(3)$; $V = 166.160(19)$ Å³ and $R_{Bragg} = 6.63$ %. The above

values are somewhat different than those reported in [16], where the a -parameter was lower and the c was higher. Moreover, the literature value of the c parameter is even slightly higher than for Ho-based sample. Similarly to HoCu₂Ge₂, the c lattice parameter exhibits a minimum at about 80 K, while the a -parameter increases with the temperature (see Fig. 1). The Ge positional parameter is constant, while the unit cell volume starts to increase at about 20 – 40 K as presented in Fig. 1.

3.7. TmCu₂Ge₂

The last measured specimen exhibits the following lattice parameters: $a = 3.99212(15)$ Å; $c = 10.32874(37)$ Å; $z_{Ge} = 0.3809(4)$; $V = 164.609(19)$ Å³ and $R_{Bragg} = 7.13$ %. The a lattice parameter is smaller than in the previous case, while the opposite holds for the c -parameter. As mentioned earlier, for the heaviest lanthanides some anomalous behaviour of the lattice parameter was observed [17]. The a -parameter follows the tendency observed for the whole series, while the c -parameter exhibits the most peculiar behaviour in comparison to other investigated compounds (see Fig. 1). Namely, there is the deepest minimum visible at rather elevated temperature of 140 K. The value of c parameter at 12 K is regained nearly at 280 K. This strongly anomalous behaviour is reflected in the thermal dependence of the unit cell volume. Although for V no minima were observed, due to a significant increase in the a -parameter, the value remained almost unchanged within the relatively broad temperature range (see Fig. 1).

4. Discussion and conclusions

The observed anomalous temperature behaviour of the c -parameter is apparent as one inspects carefully the behaviour of some reflections. For instance, in Fig. 2 the thermal dependences of 002, 110, 103 and 004 lines recorded for TmCu₂Ge₂ are presented. The expected expansion of the lattice parameter can be noticed only for the reflection related to the a -parameter (110), namely, its position shifts toward low angles as temperature rises. Contrarily, the positions of 002 and 004 reflections start to move to the high angles, then they

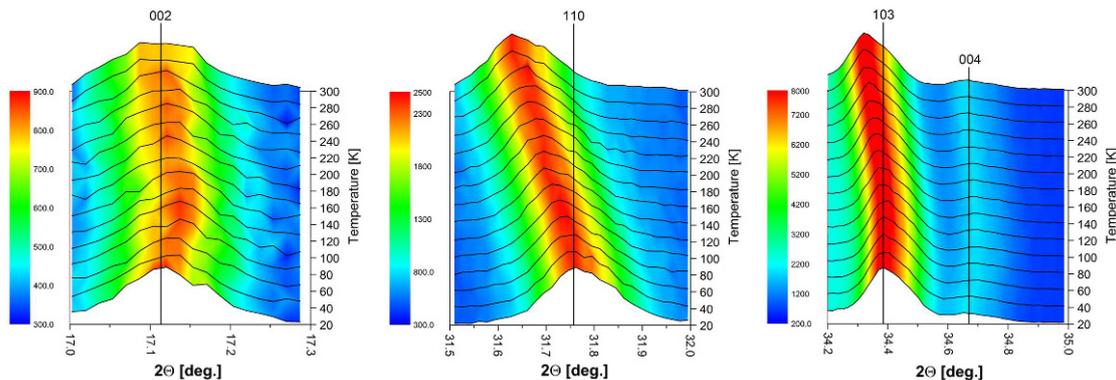


Fig. 2. Thermal dependence of some representative reflections for $TmCu_2Ge_2$.

shift in the opposite direction, regaining its initial positions at temperatures of about 280 K. Apart from above, the broadening of the reflections due to thermal oscillations is evidenced as temperature is enhanced.

As mentioned in the introduction, the anomalous behaviour of RCu_2Ge_2 compounds was attributed to quadrupolar effects [15]. The $LaCu_2Ge_2$, for which the influence of quadrupolar effects is irrelevant, exhibits well-visible anomaly of the c -lattice parameter resembling the scenario for other RCu_2Ge_2 compounds. Moreover, we made auxiliary measurements of isostructural $LaNi_2Ge_2$ and again a well-defined minimum of the c -lattice parameter at about 60 K was visible. Such kind of anomalous behaviour has been evidenced for $GdCu_2Ge_2$, however it has been just above uncertainty level. Apart from above, the character of the observed anomalies is very smooth and it is not likely to be due to any phase transition. All these facts hint at an origin of such behaviour different than quadrupolar effects.

Typically, some anomalous behaviour of lattice parameter is attributed to crystal field effects [18–20]. However, such explanation cannot be applied to samples where the orbital momentum of the rare earth is vanishing (La, Gd). Crystal field effects certainly contribute to the thermal behaviour of both lattice parameters, in particular to the changes in the slope of the relevant curves (eg. a -parameter for $HoCu_2Ge_2$), while this seems to be a secondary effect only. Taking into account that such anomaly was observed for all investigated samples, another

scenario must be taken into account. The magnetic ordering of rare earth sublattice takes place at very low temperatures (less than 13 K), hence, no influence on the mid-temperature range could be expected.

The anomalous behaviour of the c -lattice parameters can be understood in terms of phononic properties. Namely, at relatively low temperatures transversal acoustic phonons may be generated, hence, the arising thermal oscillations will lead to lattice contraction in the direction parallel to the direction of phonons propagation. This scenario is possible in strongly anisotropic systems, where optical modes are populated at higher temperatures. In tetragonal 1:2:2 compounds these conditions are fulfilled, apart from the high anisotropy resulting in lifting of degeneracy of acoustic modes, the lack of low-frequency optical branches was observed [21].

As a consequence of anisotropic lattice expansion, the c/a ratio exhibits some lowering of its value with temperature rise, as can be inferred from Fig. 3. The relative change of this parameter is strictly related to deepness of the c -axis anomaly, therefore its variation is more pronounced for $TmCu_2Ge_2$ than for other samples. The positional Ge parameter was found to be nearly constant within the entire investigated temperature range. Only for $GdCu_2Ge_2$ some statistically important changes of this parameter were evidenced. As mentioned in the previous section, the lanthanide contraction is obeyed only for the a -lattice parameter. For the c -parameter some peculiar behaviour was noticed (see Table 1), as this constant

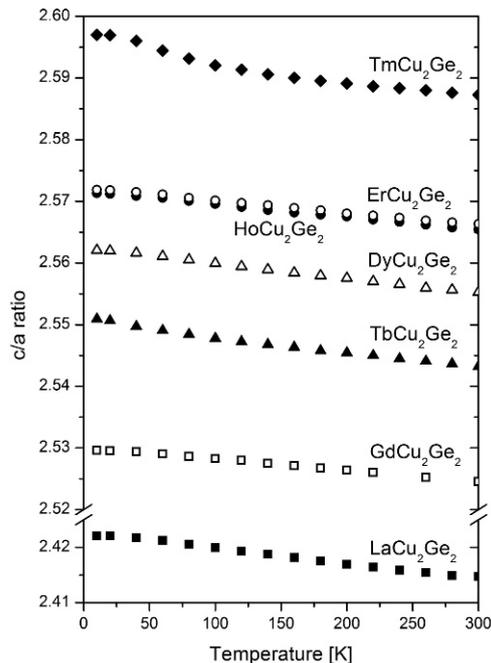


Fig. 3. Temperature variation of the c/a ratio for all investigated compounds.

systematically increases with the filling of the 4f shell (except ErCu_2Ge_2). On the other hand, the unit cell volume does not exhibit any unexpected anomalies, as it decreases with subsequent lanthanides. The latter can be well understood as one compares the relative change of both parameters.

Table 1. Lattice parameters and unit cell volume at 300 K for RCu_2Ge_2 compounds. Standard deviation are given in parentheses.

Compound	a [Å]	c [Å]	V [Å ³]
LaCu_2Ge_2	4.21539(15)	10.17878(37)	180.871(20)
GdCu_2Ge_2	4.06414(15)	10.26015(38)	169.469(20)
TbCu_2Ge_2	4.04258(13)	10.28130(34)	168.023(18)
DyCu_2Ge_2	4.02856(16)	10.29413(37)	167.066(21)
HoCu_2Ge_2	4.01707(14)	10.30555(36)	166.299(17)
ErCu_2Ge_2	4.01549(15)	10.30504(37)	166.160(19)
TmCu_2Ge_2	3.99212(15)	10.32874(37)	164.609(19)

In this work, we have addressed an issue of anomalous thermal dependence of the lattice parameter in well-known RCu_2Ge_2 family. We

have proposed that this behaviour originates from phonon properties of 1:2:2 compounds. To verify our hypothesis, inelastic neutron scattering on single crystals, non-ambient studies of Laue diffraction (with precise determination of the Debye-Waller factors) and finally *ab initio* calculations of phonon dispersion would be highly desirable.

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