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# A study on the antiferromagnetic behavior of the hydride CeRuGeH adopting the ZrCuSiAs-type structure

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## Abstract

The non-magnetic heavy fermion behavior of CeRuGe is destroyed by hydrogen insertion. The resulting hydride CeRuGeH, investigated by magnetization, thermoelectric, electrical resistivity and specific heat measurements, exhibits an antiferromagnetic ordering below  $T_N = 4.0(2)$  K weakly influenced by the Kondo effect. Below  $T_N$ , a metamagnetic double transition induced by an applied magnetic field was evidenced for CeRuGeH. This hydride presents a simple field–temperature phase diagram in comparison to that determined for the equivalent compound CeRuSiH.

## 1. Introduction

Contrary to the heavy fermion non-magnetic compound CeRu<sub>2</sub>Si<sub>2</sub> [1] and the ternary germanide CeRu<sub>2</sub>Ge<sub>2</sub> exhibiting a double transition from a paramagnetic to an antiferromagnetic and then a ferromagnetic state [2, 3], which have been intensively investigated, few studies have looked at the equiatomic systems CeRuSi and CeRuGe. This is mainly due to problems of synthesis, since CeRu<sub>2</sub>Si<sub>2</sub> and CeRu<sub>2</sub>Ge<sub>2</sub> often occur as by-products. CeRuSi and CeRuGe crystallizing in the tetragonal CeFeSi-type present a paramagnetic behavior down to 4.2 K [4]. Moreover, the investigation of these equiatomic compounds by specific heat ( $C_p$ ) measurements reveals their heavy fermion character [5, 6]: at  $T \rightarrow 0$  K, the Sommerfeld coefficient  $\gamma$  takes the values 0.18 and 0.15 J mol<sup>-1</sup> K<sup>-2</sup> for CeRuSi and CeRuGe, respectively. Also, the occurrence of a broad maximum around 5 K in the  $C_p/T = f(T)$  curves suggests the existence of magnetic interactions below this temperature [6]. The results indicate that CeRuSi and CeRuGe are close to a three-dimensional magnetic ordering.

Recently, it was shown that CeRuSi absorbs hydrogen; the resulting hydride CeRuSiH presents a unit cell volume higher (+8.1%) than that determined for the initial ternary silicide [7, 8]. Moreover, CeRuSiH exhibits two antiferromagnetic transitions at  $T_{N1} = 7.5(2)$  and  $T_{N2} = 3.1(2)$  K. Below  $T_{N1}$ , neutron powder diffraction revealed a collinear magnetic structure with a propagation vector of  $\mathbf{k} = (k_x < 1/3, k_x, 1/2)$  and an increase of  $k_x$  when the temperature decreases until  $T_{N2}$ , where the sequence incommensurate  $\rightarrow$  commensurate for the magnetic structure occurs [9]. The transition heavy fermion (CeRuSi)  $\rightarrow$  antiferromagnet (CeRuSiH), which results from a decrease of the influence of the Kondo effect induced by the hydrogen insertion, can be well understood in terms of the classical Doniach diagram [7, 10]. The hydrogenation plays a role opposite to the pressure, H shifts the compound towards the left part of this diagram and magnetic ordering appears. These results, supported by the theoretical analysis of the chemical bonding properties, suggest that in CeRuSiH, bonding effects of hydrogen do not dominate over unit cell expansion [11]. Finally, a recent investigation of CeRuSiH by magnetization measurements under hydrostatic pressure  $P$ , showed that  $T_{N1}$  and  $T_{N2}$  increase with  $P$  [12]. In other

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words, the hydrostatic pressure shifts the physical properties of CeRuSiH from the left towards the center of the Doniach diagram.

With this in mind, it would be interesting to study the influence of hydrogenation on the magnetic properties of the heavy fermion non-magnetic ternary germanide CeRuGe [6]. We report here on the investigation of the new hydride CeRuGeH by magnetization, electrical resistivity, thermoelectric power, and specific heat measurements. We discuss these physical properties in relation to those determined for CeRuSiH.

## 2. Experimental details

The starting materials for the synthesis of CeRuGe were sublimed cerium ingots (Smart elements), ruthenium powder (Heraeus, around 200 mesh), and germanium lumps (Wacker), all with stated purities better than 99.9%. In a first step, small pieces of the cerium ingots were arc-melted to small buttons under an atmosphere of about 600 mbar argon. The argon was pre-purified over a titanium sponge (900 K), silica gel, and molecular sieves. Then, the cerium ingot was mixed with ruthenium (cold-pressed to a pellet) and pieces of the germanium lumps and arc-melted under the same conditions. The melting procedure was repeated three times in order to ensure homogeneity. The total weight losses after the arc-melting were always smaller than 0.5%.

The sample was checked by Guinier powder patterns (imaging plate detector, Fujifilm BAS-1800) with Cu K $\alpha_1$  radiation and  $\alpha$ -quartz ( $a = 491.30$  and  $c = 540.46$  pm) as an internal standard. After the arc-melting procedure, the sample consisted mainly of CeRu<sub>2</sub>Ge<sub>2</sub> as well as further by-products. An almost CeRu<sub>2</sub>Ge<sub>2</sub>-free sample was obtained after annealing the arc-melted sample for 1 month at 1170 K in an evacuated silica tube.

A hydrogen absorption experiment was performed using the apparatus described previously [13]. An ingot of CeRuGe was heated under vacuum at 523 K for 12 h and then exposed for two days to 4 MPa of hydrogen gas at the same temperature. The amount of inserted H was determined volumetrically by monitoring pressure changes in a calibrated volume. Under the experimental conditions described above, the ternary germanide absorbs hydrogen; the hydrogenation induces decrepitation into small grains of the starting ingot. The molar amount of hydrogen inserted is 1.0(1) per CeRuGe formula unit. The hydride formed is stable in air and its H-content is not affected by exposure under vacuum for a temperature of less than 300 K.

X-ray powder diffraction with the use of a Philips 1050 diffractometer (Cu K $\alpha$  radiation) was applied for the characterization of the structural type and for the phase identification of the hydride. The unit cell parameters were determined by a least-squares refinement method using silicon (5N) as an internal standard.

For electrical resistivity and thermoelectric power measurements, the hydride CeRuGeH was compacted at room temperature (compactness  $\approx 80\%$ ) in order to form a polycrystalline pellet ( $\varnothing = 6$  mm and thickness  $\approx 3$  mm)

and then heated for two days at 523 K under hydrogen pressure (4 MPa). After this thermal treatment, which improves the mechanical behavior, the pellet was checked by x-ray diffraction; no structural change was evidenced. Thermoelectric power measurements were performed on this pellet using a dynamic method. Details of the cell used and measurement methods were described previously [14]. For electrical resistivity measurements, a bar of  $1.5 \times 1.5 \times 5$  mm<sup>3</sup> was cut from the pellet. The measurements were carried out above 4.2 K using the standard dc four-probe method with silver paint contacts and a current intensity of 10 mA (*due to the presence of microcracks in the sample, the absolute value of  $\rho(T)$  could not be determined accurately; for this reason, a reduced representation  $\rho(T)/\rho(270$  K) is chosen*). Finally, magnetization measurements were performed on part of the powered pellet using a superconducting quantum interference device magnetometer in a temperature range of 1.8–300 K and applied fields up to 4.6 T. Similar measurements were performed on the initial ternary germanide.

The magnetic measurements performed at 2 K with magnetic flux densities up to 8 T were carried out on a Quantum Design Physical Property Measurement System (PPMS). Therefore, the hydride sample was enclosed in a thin-walled gelatin capsule.

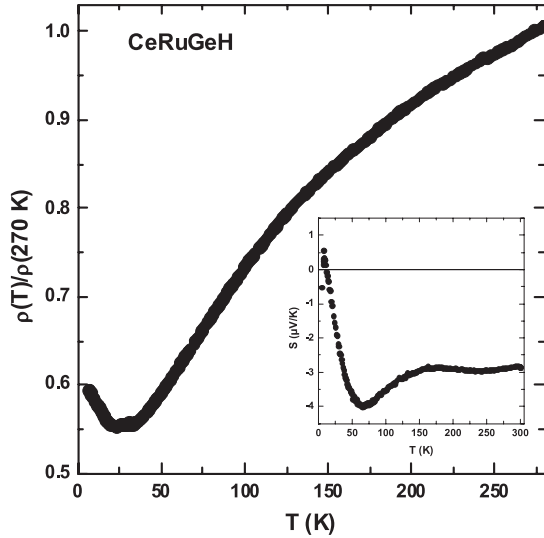
Heat capacity measurements on the hydride CeRuGeH were performed by a relaxation method with a Quantum Design PPMS system and using a two-tau model analysis. Data were taken in the 2–40 K temperature range. For these latter measurements, the sample was a plate of weight 30.5 mg obtained from the same pellet used for the other physical characterization.

## 3. Results and discussion

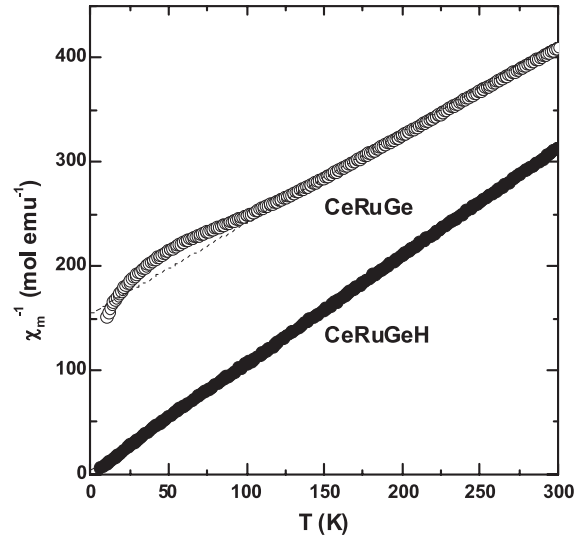
The crystal structure of CeRuGeH adopts the same space group type ( $P4/nmm$ ) as the initial ternary germanide CeRuGe but the hydride crystallizes in the tetragonal ZrCuSiAs-type structure as observed previously for CeRuSiH [7–9]. In this structure, the H atoms occupy the [Ce<sub>4</sub>] tetrahedral sites. Thus, CeRuSiH and CeRuGeH belong to the large family of ZrCuSiAs compounds; an overview of the crystal chemistry and chemical bonding of these exciting materials is given in [15].

The hydrogenation of CeRuGe causes a pronounced anisotropic expansion of the unit cell; the  $a$ -parameter decreases from 4.275 to 4.201(1) Å (−1.7%) whereas the  $c$ -parameter increases strongly from 6.871 to 7.542(2) Å (+9.8%). In other words, the hydrogenation of CeRuGe involves a 6.0% expansion of the unit cell volume. These results are comparable to those reported during the hydrogenation of CeRuSi where a higher increase of the unit cell volume (8.1%) was reported [7]. Also, the unit cell volume of CeRuGeH (133.10 Å<sup>3</sup>) is higher than that of CeRuSiH (131.24 Å<sup>3</sup>), in agreement with the bigger atomic radius of germanium compared to that of silicon.

In CeRuGeH, the interatomic distances  $d_{\text{Ce-H}} = 2.458$  Å between Ce and H atoms is higher than that existing for CeRuSiH ( $d_{\text{Ce-H}} = 2.447$  Å). Also, all the  $d_{\text{Ce-Ce}}$  distances



**Figure 1.** Temperature dependence, above 4.2 K, of the reduced electrical resistivity of CeRuGeH. The inset presents, for this hydride, the temperature dependence of its thermoelectric power  $S$ .



**Figure 2.** Temperature dependence of the reciprocal magnetic susceptibility  $\chi_m^{-1}$ , measured with an applied field of 3 T, for CeRuGe and its hydride. The dashed lines present the Curie–Weiss law.

(3.918 and 4.201 Å) are greater than that reported for CeRuSiH (3.900 and 4.180 Å) [7]. This last result suggests a decrease of the RKKY magnetic interaction in the sequence CeRuSiH → CeRuGeH.

Above 4.2 K, the temperature dependence of the reduced electrical resistivity  $\rho(T)/\rho(270\text{ K})$  of the hydride CeRuGeH reveals several characteristics (figure 1): (i) a downward curvature around 150–200 K (such behavior, which is similar to that reported previously for CeRuSiH [7], is expected for Kondo-type interactions in the presence of crystal field effects [16]) and (ii) a minimum around 20–30 K, suggesting the influence of the Kondo effect. The electrical properties of CeRuGeH are different from those determined for the initial ternary germanide CeRuGe. The resistivity of this last intermetallic increases in a Kondo-like manner when the temperature decreases from 300 to about 90–100 K and exhibits a rapid decrease below 90–100 K [6]. A comparison between the electrical properties of CeRuGe and its hydride suggests that the hydrogenation diminishes the influence of the Kondo effect.

In the same way, the temperature dependence of the thermoelectric power  $S$  of CeRuGeH is similar to that reported for CeRuSiH (inset of figure 1).  $S$  is small and negative with a minimum around 65 K, except at very low temperature where  $S$  presents a very small positive peak near 7 K.

Figure 2 presents the temperature dependence of the reciprocal magnetic susceptibility  $\chi_m^{-1}$  of CeRuGe and its hydride. An appreciable increase in the  $\chi_m$  value of the hydride is observed relative to that of CeRuGe.

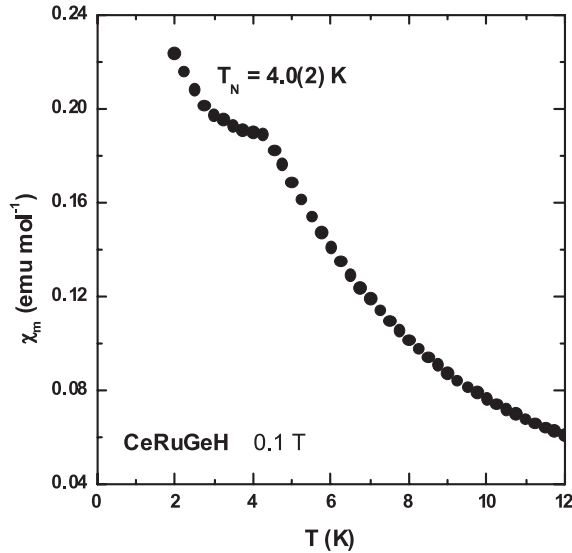
The curve  $\chi_m^{-1}$  versus  $T$  concerning CeRuGe follows a Curie–Weiss law above 150 K, and below 150 K exhibits a positive deviation from this law and finally decreases below 50 K in agreement with the presence of a small amount of free  $\text{Ce}^{3+}$  ion stabilized lattice defects or a trace of some paramagnetic impurities such as CeRu<sub>2</sub>Ge<sub>2</sub>. The behavior below 150 K can be ascribed to the existence of local spin

fluctuations as a result of the occurrence of Kondo interactions as suggested by the large negative value of the paramagnetic Curie temperature ( $\theta_p = -176\text{ K}$ ) deduced from the Curie–Weiss law. These data obtained here for CeRuGe are in agreement with those reported earlier [6].

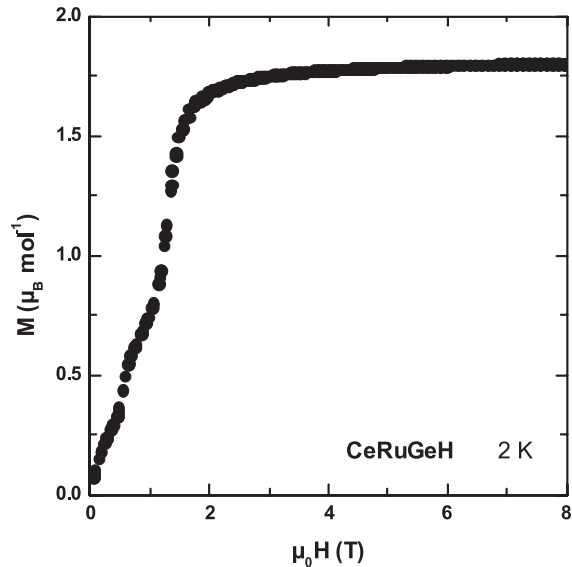
On the contrary, above 50 K the  $\chi_m^{-1}$  versus  $T$  curve relative to the hydride CeRuGeH can be fitted with a Curie–Weiss law, giving a small  $\theta_p = -3\text{ K}$  paramagnetic Curie temperature and  $\mu_{\text{eff}} = 2.64\ \mu_B\ \text{mol}^{-1}$  as effective moment. This last value is close to that calculated for a free  $\text{Ce}^{3+}$  ion ( $2.54\ \mu_B$ ). In other words, the cerium is purely trivalent in the hydride. Also, the hydrogenation of the ternary CeRuGe induces a great change of the  $\theta_p$  temperature from  $-176$  to  $-3\text{ K}$  suggesting a decrease of the influence of the Kondo effect.

The presence of a shoulder at  $T_N = 4.0(2)\text{ K}$  in the temperature dependence of the magnetic susceptibility  $\chi_m$  of the hydride CeRuGeH (figure 3) suggests an antiferromagnetic ordering of the Ce magnetic moments. This magnetic ordering is further corroborated by the field-dependent behavior of the magnetization  $M$  taken below  $T_N$  (figure 4). For instance at 2 K and up to  $\mu_0 H = 8\text{ T}$ ,  $M$  versus  $\mu_0 H$  is seen to show two steplike features at critical fields 0.53(2) and 1.27 T (these values are deduced from the derivative  $\partial M/\partial \mu_0 H$  versus  $\mu_0 H$ ). This behavior suggests the occurrence of a magnetic transition induced by the applied magnetic field as observed in many antiferromagnets as CeRuSiH (spin-flip or spin-flop transition) [7]. After the second field induced transition, the magnetization reaches a value of  $1.81(3)\ \mu_B\ \text{mol}^{-1}$ , which is larger than the mean powder average for any of the doublets expected for a localized  $\text{Ce}^{3+}$  ion ( $g_J \times J = 2.14\ \mu_B$ ) in a tetragonal local symmetry [17], suggesting some preferred orientation. This very large magnetization indicates the absence of any influence of the Kondo effect.

The specific heat  $C_p$  of CeRuGeH has been measured at zero magnetic field (figure 5). The curve  $C_p$  versus  $T$  exhibits:

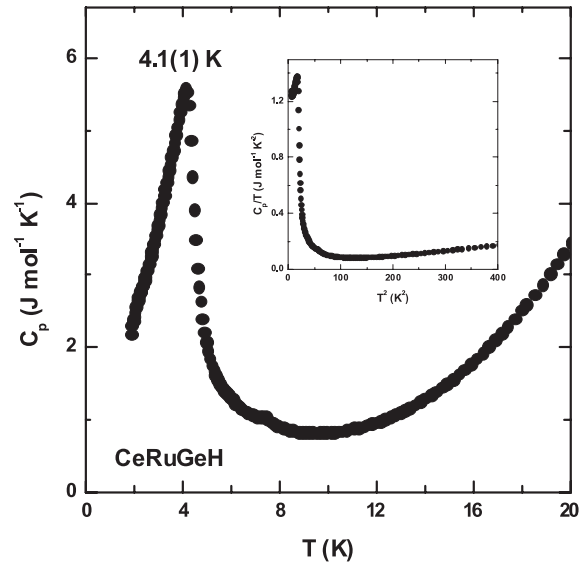


**Figure 3.** Temperature dependence of the magnetic susceptibility  $\chi_m$ , measured with an applied field of 0.1 T, for CeRuGeH.



**Figure 4.** Field dependence at 2 K of the magnetization of CeRuGeH.

(i) a small step around 7.4 K which can be ascribed to the presence of traces of the impurity phase  $\text{CeRu}_2\text{Ge}_2$  [2, 3]. At its ferromagnetic transition ( $T_C = 7.40$  K), the  $C_p/T$  versus  $T$  curve for this last ternary germanide shows a huge peak [3]; (ii) a peak at about 4.1(1) K associated with the occurrence of the antiferromagnetic transition detected for CeRuGeH. This temperature agrees with the Néel temperature reported above by magnetization measurements. Linear fitting of  $C_p/T$  versus  $T^2$  (according to  $C_p/T = \gamma + \beta T^2$ ) in the range from 20 to 12 K (inset of figure 5) yields an electronic coefficient  $\gamma = 19$   $\text{mJ mol}^{-1} \text{K}^{-2}$  smaller than that reported for CeRuGe ( $\gamma = 150$   $\text{mJ mol}^{-1} \text{K}^{-2}$ ) [6]. This strong decrease of  $\gamma$  indicates that the hydrogenation of CeRuGe destroys its heavy fermion behavior.



**Figure 5.** Temperature dependence, above 2 K, of the specific heat  $C_p$  for CeRuGeH. The inset presents the  $C_p/T$  versus  $T^2$  curve.

At  $T_N = 4.0(2)$  K, the magnetic entropy reaches  $S_m = 4.70$   $\text{J mol}^{-1} \text{K}^{-1}$  or  $0.82R \ln 2$ , which is greater than that obtained for the hydride CeRuSiH ( $S_m = 3.473$   $\text{J mol}^{-1} \text{K}^{-1}$  or  $0.60R \ln 2$ ) [7].  $S_m$  of CeRuGeH is weakly smaller than  $R \ln 2 = 5.76$   $\text{J mol}^{-1} \text{K}^{-1}$ , the value expected for a doublet ground state of  $\text{Ce}^{3+}$ . This reduction can be attributed to the presence of the impurity ternary germanide  $\text{CeRu}_2\text{Ge}_2$  in the sample.

#### 4. Conclusion

In summary, we have shown that the hydrides CeRuSiH and CeRuGeH, deriving from the heavy fermion systems CeRuSi and CeRuGe, present at low temperature an antiferromagnetic behavior little influenced by the Kondo effect. In comparison to CeRuSiH, above 2 K CeRuGeH exhibits only one antiferromagnetic ordering with a smaller Néel temperature. These hydrides crystallize in a structure isotypic to the phosphide oxides CeRuPO and CeOsPO; these last compounds are respectively ferromagnetic ( $T_C = 15$  K) and antiferromagnetic ( $T_N = 4.5$  K) [18]. In these two classes of materials, the  $[\text{Ce}_4]$  tetrahedra are filled by oxygen or hydrogen atoms. It is suggested that other investigations such as electronic structure calculation or  $^1\text{H}$  nuclear magnetic resonance (NMR) are performed on CeRuSiH and CeRuGeH in order to classify these compounds as intermetallic or hydride materials. A similar large influence of hydrogenation on the magnetic properties has recently been observed for NdMnSiH [19].

#### Acknowledgments

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## References

- [1] Besnus M J, Kappler J P, Lehmann P and Meyer A 1985 *Solid State Commun.* **55** 779
- [2] Raymond S, Haen P, Calemczuk R, Kambe S, Fak B, Lejay P, Fukuhara T and Flouquet J 1999 *J. Phys.: Condens. Matter* **11** 5547
- [3] Wilhelm H, Alami-Yadri K, Revaz B and Jaccard D 1999 *Phys. Rev. B* **59** 3651
- [4] Welter R, Venturini G, Malaman B and Ressouche E 1993 *J. Alloys Compounds* **202** 165
- [5] Rebelsky L, Reilly K, Horn S, Borges H, Thompson J D, Willis J O, Aikin R, Caspari R and Bredl C D 1988 *J. Appl. Phys.* **63** 3405
- [6] Sereni J G, Caroca-Canales N, Kumar M, Oeschler N, Gomez Berisso M and Geibel C 2009 *J. Phys. Conf. Ser.* at press
- [7] Chevalier B, Gaudin E, Tencé S, Malaman B, Rodriguez Fernandez J, André G and Coqblin B 2008 *Phys. Rev. B* **77** 014414
- [8] Chevalier B, Tencé S, Gaudin E, Matar S F and Bobet J-L 2009 *J. Alloys Compounds* **480** 43
- [9] Tencé S, André G, Gaudin E and Chevalier B 2008 *J. Phys.: Condens. Matter* **20** 255239
- [10] Doniach S 1976 *Proc. Int. Conf. on Valence Instabilities and Related Narrow-Band Phenomena* ed R D Park (New York: Plenum) p 168
- [11] Matar S F 2007 *Phys. Rev. B* **75** 104422
- [12] Rodriguez Fernandez J, Rojas D P, Gomez Sal J C, Tencé S and Chevalier B 2009 *J. Phys. Conf. Ser.* at press
- [13] Bobet J-L, Pechev S, Chevalier B and Darriet B 1998 *J. Alloys Compounds* **267** 136
- [14] Dordor P, Marquestaut E and Villeneuve G 1980 *Rev. Phys. Appl.* **15** 1607
- [15] Pöttgen R and Johrendt D 2008 *Z. Naturf.* **63b** 1135
- [16] Cornut B and Coqblin B 1972 *Phys. Rev. B* **5** 4541
- [17] Fischer G and Herr A 1990 *Phys. Status Solidi b* **159** K23
- [18] Krellner C, Kini N S, Brüning E M, Koch K, Rosner H, Nicklas M, Baenitz M and Geibel C 2007 *Phys. Rev. B* **76** 104418
- [19] Tencé S, André G, Gaudin E, Bonville P, Al Alam A F, Matar S F, Hermes W, Pöttgen R and Chevalier B 2009 *J. Appl. Phys.* **106** 033910