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# Electronic structure and magnetic properties of the magnetically ordered intermediate valent $Ce_5RuGe_2$

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ABSTRACT

We report here a comprehensive investigations of the band structure, magnetic properties, electrical transport, and specific-heat for ternary compound $Ce_5RuGe_2$ that crystallize in orthorhombic $Y_2HfS_5$-type structure. The results show a complex magnetic structure with the field-induced metamagnetic transitions in coexistence with spin-glass-like phase, displayed in the magnetic $H-T$ phase diagram. Simultaneously, a combined experimental and theoretical study based on x-ray photoelectron spectroscopy (XPS) data together with *ab initio* band structure calculations indicate a mixed valence of Ce due to strong hybridization between Ce 4*f* states and conduction band. The obtained magnetic ground state of $Ce_5RuGe_2$, resulting from localized *f*-electron states and accompanying strong hybridization effect leading to valence instability of cerium ions are rarely observed for Ce-based intermetallic compounds.


## 1. Introduction

A number of Ce-based intermetallic compounds show several distinct ground states which depend crucially on the competition between Ruderman-Kittel-Kasuya-Yosida (RKKY) and Kondo interactions, modified by the crystalline electric field (CEF). The first effect leads to long range magnetic order of the localized Ce magnetic moments, while the latter one suppresses the Ce 4*f* magnetic moments and leads to the Abrikosov-Suhl resonance manifesting itself as a narrow peak in a quasi-particle density of states (DOS) near the Fermi level. The result of the competition between these interactions was first discussed by Doniach on the basis of the Kondo-lattice model Hamiltonian [1]. The simple phase diagram exhibits the magnetic ordering temperature $T_{RKKY}$ vs $J_{fc}N(\varepsilon_F)$, where $J_{fc} \sim V_{fc}$ represents the exchange interaction between 4*f* and conduction electrons, $N(\varepsilon_F)$ is the DOS at the Fermi level and $V_{fc}$ is the on-site hybridization energy. In the Kondo-lattice limit, the stability of various ground states is, however, strongly dependent on the bare *f*-level position in the conduction band, $\varepsilon_f$, the number of electrons per atom, $n_e$, and the magnitude of the on-site Coulomb interaction $U$ within the shell [2]. These band structure properties are not included in the Doniach model, which does not explain the character of the low-temperature magnetic ground state. Because magnetic ground state in Ce metallic compounds is evidently susceptible to electronic interaction since the 4*f* electron states of Ce can be variably bound in respect to the Fermi surface ($\varepsilon_F$), the magnetic phases are better interpreted within the periodic Anderson model [2]. The calculated mean-field magnetic phase diagram $V_{fc}-n_e$ with the Kondo-compensated phases gave a good qualitative interpretation of experimental results for the series of various Ce ternary intermetallics (see, e.g., Refs. [3–5]). A strong hybridization with conduction electrons generally decreases the localization of the 4*f*-electron states, and results in appearance of a non-magnetic intermediate valence behavior. In this work the title compound $Ce_5RuGe_2$ is magnetically ordered and is found to display mixed valence phenomena for Ce ions. The fluctuating (or mixed) valence phenomena pose challenging problems of strongly correlated systems, especially those with low-temperature magnetic order. In the course of our systematic investigations on $CeM_5Ge_2$, where $M$ is *d*-electron type metal we document partial filling of the 4*f*-shell with characteristic valence fluctuation behavior (e.g., in $Ce_2Rh_3Ge$ [6,7]) in coexistence with magnetic order. In this paper we report the first measurements of electronic structure, magnetic, specific heat, and electrical transport properties of $Ce_5RuGe_2$. We believe that our research of dichotomous 4*f* electron properties (localization/delocalization) in rare case of magnetically ordered intermediate valent $Ce_5RuGe_2$ compound

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will stimulate further in-depth studies.

## 2. Experimental and calculations details

Polycrystalline $Ce_5RuGe_2$ sample was prepared by arc-melting constituent elements with purities higher than 99.9%, in arc furnace under protective argon atmosphere. Afterwards, the sample was remelted several times, wrapped in tantalum foil and annealed for one week at 870°C. The sample was examined by x-ray diffraction (XRD) analysis and found to have an orthorhombic, $Y_2HfS_5$-type structure within space group *Pnma*. The X-ray diffraction pattern was obtained using a diffractometer (PANalytical Empyrean) equipped with the Cu K$\alpha$ source. The obtained diffraction patterns were analysed with the Rietveld refinement method by programs Maud [8,9] and Fullprof [10] with the pseudo-Voigt diffraction line shape.

Electrical resistivity, specific heat and magnetic ac susceptibility measurements were carried out using the Quantum Design PPMS (physical properties measurement system) platform. Magnetic dc susceptibility and magnetization was measured using a Quantum Design superconducting quantum interference device (SQUID) magnetometer in the field up to 7 T.

The XPS spectra were obtained with monochromatized Al K$\alpha$ radiation at the room temperature using a Physical Electronic PHI 5700/600 ESCA spectrometer. In order to obtain good quality XPS spectra the polycrystalline sample was cleaved and measured in the vacuum of about $10^{-10}$ Torr.

The electronic structure of $Ce_5RuGe_2$ was calculated using the FPLO method (FPLO5.50 computer code [11–15]) for the experimental lattice parameters. Calculations were carried out in spin resolved, scalar relativistic way without Coulomb correlations taken into account for rare-earths and transition elements. The additional 4*f* correlations taken into account within LSDA+U approach for rare earth intermetallics typically increase magnetic moments even up to 1 $\mu_B$ for very small *U* parameter (c.f. Ref. [16,17]). Here we are interested in detailed analysis of magnetic properties of $Ce_5RuGe_2$ compound, which has four inequivalent Ce sites, each one showing different magnetic moment. Additional correlations would increase already significant magnetic moments and would diminish the differences between them. Our thorough analysis of the magnetization is based on this difference, hence for this system we used just plain LSDA approach. The spin orbit coupling has not been considered in the current study. We considered (6*s*,6*p*,5*d*) as valence states for Ce; (5*s*,5*p*,4*d*) for Ru and (4*s*,4*p*,3*d*) for Ge. Following states were considered as semicore states: (4*f*,5*s*,5*p*) states for Ce; (4*s*, 4*p*) for Ru and (3*s*, 3*p*) for Ge. The number of *k*-points in the irreducible wedge of the Brillouin zone was 64.

## 3. Results and discussions

### 3.1. X ray diffraction analysis

Fig. 1 shows the XRD pattern for $Ce_5RuGe_2$. The lattice parameter values of the *Pnma* space group obtained by the Rietveld refinement method are as follows: $a = 12.2756$ Å, $b = 8.9090$ Å, and $c = 8.0253$ Å for a bulk $Ce_5RuGe_2$ sample, which are in good agreement with those presented in Ref. [18]. The Rietveld analysis also indicates the presence of less than 8% impurity polymorphic phase of $Ce_5RuGe_2$ with hexagonal $P6_3/mcm$ crystallographic structure having the lattice parameters: $a = 8.8806$ Å and $c = 6.5846$ Å. The presence of 3% of the similar polymorphic phase has also been reported for izostructural compound $Ce_5PdGe_2$ [5]. The atomic positions obtained from Rietveld refinement for the both: bulk and impurity polymorphic phases of $Ce_5RuGe_2$ are presented in Table 1. The final least-squares refinement cycle gave the weighted-profile *R* factor $R_w = 1.68$ ($R_w = \left\{\sum_i w_i[y_i(obs) - y_i(calc)]^2\right] \Big/ \sum_i w_i y_i(obs)^2\right\}^{1/2} \times 100\%$, where $y_i$ is a value of observed or calculated intensity, and $w_i$ is the weight [19]). Table 2 lists the nearest interatomic distances between different Ce atoms in the $Ce_5RuGe_2$ unit cell.

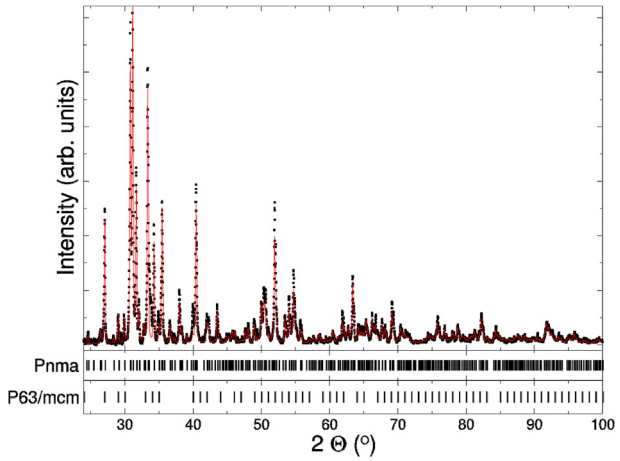


**Fig. 1.** The observed (red points) and calculated (black line) X-ray diffraction pattern for the $Y_2HfS_5$-type (*Pnma*) $Ce_5RuGe_2$ compound. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The structure of $Ce_5RuGe_2$ is shown in Fig. 2.

### 3.2. Electronic structure of $Ce_5RuGe_2$; experimental (XPS) evidence for $Ce4f^0$ states

On the base of the band structure calculations carried out in a fully relativistic way and the core level and valence band XPS spectra we will interpret the results determined from the specific heat, electrical transport and the comprehensive magnetic investigations. The most important results of these investigations are following. (*i*) The ground state of $Ce_5RuGe_2$ is calculated as strongly magnetic. The calculated magnetic moment of Ce ions depends on its atomic coordinates, and is 0.652 $\mu_B$ for Ce1, 0.758 $\mu_B$ for Ce2, 0.671 $\mu_B$ for Ce3, and 0.815 $\mu_B$ for Ce4, respectively. The calculated magnetic moment of Ru and Ge atoms is respectively, −0.034 $\mu_B$ and −0.047 $\mu_B$. The negative magnetic moment of Ru and Ge leads to the diamagnetic contribution to magnetic susceptibility $\chi$ (will be discussed). Fig. 3 shows the valence band (VB) XPS spectra and the calculated total density of states per formula. This comparison

**Table 1**
Atomic coordinates for the $Ce_5RuGe_2$ compound [$Y_2HfS_5$-type structure (*Pnma*) for the bulk sample, and the $Mn_5Si_3$-type ($P6_3/mcm$) impurity phase].

| Atom | Wyckoff position | *x* | *y* | *z* |
|---|---|---|---|---|
| *Pnma* | | | | |
| Ce1 | 8*d* | 0.0711 | 0.5270 | 0.3156 |
| Ce2 | 4*c* | 0.00 | 0.25 | 0.0345 |
| Ce3 | 4*c* | 0.2046 | 0.25 | 0.6463 |
| Ce4 | 4*c* | 0.2860 | 0.25 | 0.1590 |
| Ru | 4*c* | 0.0239 | 0.25 | 0.4318 |
| Ge | 8*d* | 0.3299 | 0.4977 | 0.4402 |
| $P6_3/mcm$ | | | | |
| Ce1 | 6*g* | 0.2456 | 0 | 0.25 |
| Ce2 | 4*d* | 0.3333 | 0.6667 | 0 |
| Ru,Ge | 6*g* | 0.6039 | 0 | 0.25 |