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Electronic Structure and Magnetic Properties of Ce_5CuPb_3 Based on *Ab Initio* Calculations

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Ce_5CuPb_3 band structure has been calculated based on two *ab initio* methods: full potential-linearized augmented plane wave implemented in WIEN2k code and full-potential local-orbital minimum-basis in FPLO code. The calculations were performed with and without spin polarization. Starting from the generalized gradient approximation we additionally tested either an orbital polarization correction and the GGA+U approach with the Coulomb repulsion energies U varied from 0 to 6.7 eV within the Ce $4f$ electron shell. The calculations confirmed possible antiparallel alignment of the magnetic moments of the cerium atoms in the low temperature phase.

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1. Introduction

Ternary rare-earth (R) plumbides R_5CuPb_3 form a wide family crystallizing in hexagonal Ti_5Ga_4-type structure with space group $P6_3/mcm$ [1], where R = Y and all lanthanides except Pm. These intermetallics are characterized by two different sites for the R ions located at 4d and 6g positions, respectively. We focus our attention on Ce_5CuPb_3 compound, which is classified as medium heavy fermion system and observed electronic specific heat is typical as found in numbers of medium electron correlated Ce compounds [2]. The magnetic measurements have shown that Ce_5CuPb_3 is a magnet with double transitions below $T_{C1} = 46$ K and $T_{C2} = 5$ K [2, 3]. The analysis of the magnetic data suggested that the origin of the transition at T_{C1} is ferromagnetic and at T_{C2} is a ferri- or an antiferromagnetic one.

The electronic band structure calculation [2] based on *ab initio* methods confirmed the magnetic ground state. Direct comparison between the total energies of the nonmagnetic case as well as the cases when ferro- and antiferromagnetic coupling between the Ce1 and Ce2 sublattices occurs has shown that the most stable was a simple ferromagnetic configuration with spins aligned along z-axis. This conclusion is contradictory with the experimental data.

The aim of this work is to give insight into the magnetic structure of the Ce_5CuPb_3 compound based on modern *ab initio* spin polarized band structure calculations allowing for better approach to the strongly correlated electron systems.

2. Details of calculations

We used experimental lattice constants ($a = 9.551$ Å, $c = 6.776$ Å) and the Wyckoff positions [2]. The unit cell is presented in Fig. 1. Calculations were performed by using the WIEN2k [4] and the FPLO [5] codes, which based on the density functional theory (DFT) [6] with the exchange-correlation functional treated in the generalized gradient approximations (GGA) of the Perdew, Burke, Ernzerhof form [7]. The FPLO calculations were performed in fully-relativistic mode, where the four-component Kohn–Sham–Dirac equation is solved, treats exactly all relativistic effects, including the spin–orbit (SO) interaction — without approximations. It is not the case for the WIEN2k code where the scalar relativistic approach was implemented with the SO interaction taken into account approximately by employing the second variational method [8]. Furthermore, to improve a description of the strongly correlated Ce $4f$ electrons by the WIEN2k code, the on-site Coulomb-repulsion energy U introduced within the GGA+U approach in the version introduced by Anisimov et al. [9]. In our calculations we used an "effective" parameter defined as $U_{\text{eff}} = U - J$, setting the exchange interaction term $J = 0$. Taking into account so-called orbital polarization (OP) term as proposed by Brooks [10] and Eriksson et al. [11] is another approach to improve discrepancy between calculated and experimental magnetic moment. A tetrahedron method [12] was employed to carry out the k-space integrations, using at least 8000 points in the Brillouin zone (BZ). The total energy was converged at a level of 10^{-6} Ry.

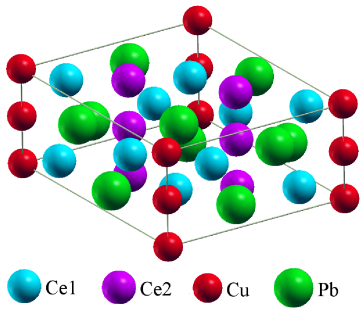

Fig. 1. The crystallographic structure of Ce_5CuPb_3.

3. Results and discussion

First, the spin polarized calculations were started for WIEN2k and FPLO code for GGA approach. Using the

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WIEN2k code we reproduced the magnetic moments obtained by Tran et al. [2] (see Table). The FPLO code gave higher values but in both cases magnetic moments on Ce1 (4d site) and Ce2 (6g site) atoms were parallel, not antiparallel as it was suggested by the experimental data [2, 3] in the low temperature phase below T_{C2}. Different environment of the cerium atoms is the cause of distinct values of magnetic moments on Ce1 and Ce2 atoms. It is difficult to compare the calculated values to the experimental ones because there is no experimental data on local moments of the cerium atoms. Only the value of magnetization is available, 0.36 μ_B/Ce atom, however, at the maximum strength of the applied magnetic field of 5 T, the magnetization does not saturate.

TABLE

The electronic and magnetic characteristics for Ce_5CuPb_3: local magnetic moments on the cerium atoms and total moments (magnetization) [μ_B/Ce atom], spin projected total densities of states (DOS) at the Fermi level (E_F) [states/(eV f.u. spin)], and the Sommerfeld specific heat coefficient γ [mJ/(mol K^2)] obtained from the calculations. In Ref. [2] spin projected values of DOS(E_F) were not available.

WIEN2k (GGA+U)	Ce1 (4d site)	Ce2 (6g site)	total (per Ce)	DOS(E_F) up	DOS(E_F) down	γ
$U = 0$	0.57	0.20	0.35	14.77	2.27	40.4
$U = 1$ eV	0.73	0.03	0.31	18.86	3.07	51.7
$U = 2$ eV	0.76	−0.20	0.18	30.46	2.52	77.8
$U = 3$ eV	0.78	−0.11	0.25	23.82	1.89	60.6
$U = 4$ eV	0.78	−0.21	0.19	26.79	1.54	66.8
$U = 5$ eV	0.78	−0.17	0.21	27.35	1.80	68.7
$U = 6$ eV	0.78	−0.22	0.18	27.81	2.12	70.6
$U = 6.7$ eV	0.71	−0.21	0.16	28.65	2.47	73.3
FPLO(GGA)	1.08	0.51	0.74	15.02	2.60	41.5
(GGA+OP)	0.27	−0.46	0.17	37.76	3.06	96.2
WIEN2k [2]	0.57	0.19	0.34	29.36		69.2
experiment [2]			0.38			250

The next step was to apply the GGA+U approach to simulate strong electron–electron correlation. The value of U, step by step, was increased form 0 to 6.7 eV, the upper limit is taken from the paper by van der Marel and Sawatzky [13] (see Table IV presenting interpolating formulae for experimental values of U and J). Figure 2 presents calculated magnetic moments (spin, orbital and resultant) on the cerium atoms. The left part shows results of WIEN2k (GGA+U) moments vs. effective parameter U. One can observe that varying U it is possible to obtain the parallel as well as antiparallel alignment of the Ce1 and Ce2 moments. The values of the cerium magnetic moments are collected in Table and presented in Fig. 2. Above $U = 2$ eV the magnetic moments on the cerium atoms saturate. Also FPLO calculations using GGA+OP approach gives consistent alignments of Ce moments with experimental data but more data is necessary to compare their values.

In Fig. 3 one can observe the dependence of DOS at the Fermi level and corresponding Sommerfeld coefficient γ in the specific heat. Ce_5CuPb_3 is a medium heavy fermion system [2] and its γ coefficient (250 mJ/(mol K^2) [2]) is much higher than the calculated ones. It is because of many-body effects which are not completely taken into account in *ab initio* calculations. So-called enhancement factor λ is in the range between 2.2 and 5.2 for WIEN2k (GGA+U) calculations, 5 and 1.6 for FPLO(GGA/GGA+OP) calculations, respectively. The main contribution to the total DOS at the Fermi level is provided by Ce atoms (about 79–85%), mainly by $4f$ electrons.

Figure 4 presents the DOS plots for WIEN2k (GGA/GGA+U) and FPLO(GGA/GGA+OP) calculations. The common feature is a large difference between spin up and down plots near the Fermi level. The black curves form a pseudo gap near E_F. The second channel of spin forms there high peaks, mainly by $4f$ electrons. Two peaks located around −3 and −3.5 eV are formed by Cu $3d$ electrons and the Pb atoms form small peak around −8 eV.

4. Summary and conclusions

In this paper we presented results of the *ab initio* band structure calculations for the Ce_5CuPb_3 compound. Two full potential methods, FPLO and WIEN2k, allowed to go beyond typical GGA/LSDA approaches and treat more correctly the electron correlations. We used either an orbital polarization correction and the GGA+U approach with the Coulomb repulsion energies U varied from 0 to 6.7 eV within the Ce $4f$ electron shell. The calculations confirmed possible antiparallel alignment of the magnetic moments of the cerium atoms in the low temperature phase.

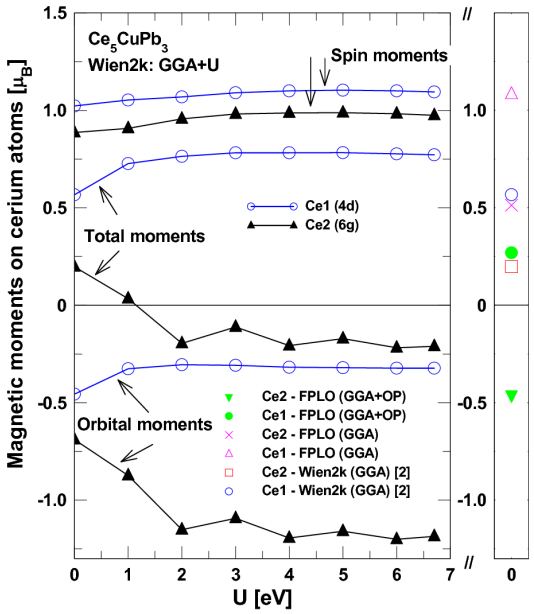

Fig. 2. The dependence of the calculated magnetic moments on the cerium atoms in Ce_5CuPb_3 on the Coulomb repulsion U parameter taken in the GGA+U approach (WIEN2k, see Table). For comparison also WIEN2k (GGA) [2] and FPLO(GGA/GGA+OP) values are drawn in the right-hand column (see Table). The magnetic moments on the Cu and Pb sites are neglected.

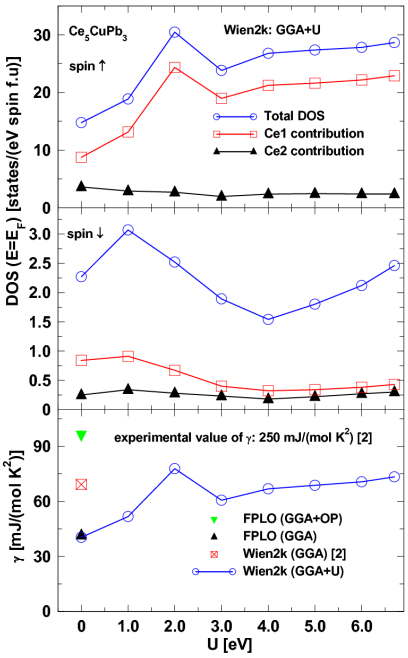

Fig. 3. The dependence of the spin projected total densities of states (DOS) at the Fermi level (E_F) [states/(eV f.u. spin)] and the Sommerfeld specific heat coefficient γ [mJ/(mol K^2)] obtained from the calculations in Ce_5CuPb_3 on the Coulomb repulsion U parameter taken in the GGA+U approach (WIEN2k, see Table). In the lowest panel, for comparison, also WIEN2k (GGA) [2] and FPLO(GGA/GGA+OP) γ values are drawn (see Table).

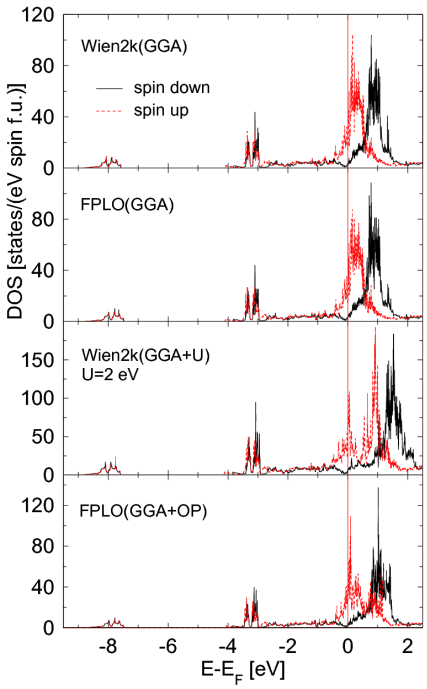

Fig. 4. The spin projected total densities of states (DOS) for Ce_5CuPb_3 based on *ab initio* calculations: WIEN2k/FPLO(GGA), WIEN2k (GGA+U) and FPLO(GGA+OP).

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