

The Ce electronic ground state in CeMn_2Ge_2 determined by ^{140}Ce PAC spectroscopy and electronic structure calculations

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Abstract

In this work a search for a $4f$ Ce ground state in CeMn_2Ge_2 is performed based on results of magnetic hyperfine field (MHF) measurements made with time differential perturbed angular correlation spectroscopy on ^{140}Ce isotope and with the aid of first-principles electronic structure calculations within the GGA + U framework. It was found that after tuning the Hubbard-like parameter U_{eff} within density-functional-theory in order to match for the observed MHF, the crystalline-field-split Γ_6 state appears as the most probable ground state. It is also shown that Γ_6 is in accordance with the known Kondo-lattice parameters in CeMn_2Ge_2 .

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PACS: 71.20.Eh; 71.70.Ch; 71.27.+a

Keywords: Magnetic hyperfine field; Ce compounds

1. Introduction

The CeMn_2Ge_2 compound belongs to a series of intermetallics generically designated as RT_2X_2 , where R is a rare-earth element, T a transition metal and X stands for an sp element such as Si, Ge, Sn or Sb. The branch of these compounds where the rare-earth is Ce exhibits a large variety of physical phenomena, including mixed valence, heavy fermion, Kondo physics, magnetism and superconductivity. A particularly interesting feature of CeMn_2Ge_2 and CeMn_2Si_2 compounds is that they are the only members of this group where magnetic moments appear exclusively at the Mn atoms, even at low temperatures, as determined by neutron diffraction measurements. While for the silicide the absence of the magnetic moment on Ce atoms is understood as due to a lacking of direct Ce–Ce magnetic interaction and anti-ferromagnetic ordering of Mn, in CeMn_2Ge_2 the small or absent magnetic moment on Ce is intriguing since the Mn atoms present a partial ferromagnetic order below $T_C = 320$ K: below this temperature the Mn atoms

order with an incommensurate ferromagnetic component along the c -axis and a helical component in the ab -plane of the tetragonal crystalline structure with space group $I4/mmm$ [1,2].

On the other hand, another interesting result was provided by recent time-differential-perturbed-angular-correlation (TDPAC) measurement on ^{140}Ce isotope that revealed the existence of a significant magnetic hyperfine field (MHF) of 39.0 ± 1.4 T at 10 K in CeMn_2Ge_2 [3], giving a strong indication that the MHF is not proportional to the magnetic moment in this case.

An interpretation of these results is reported in Ref. [4] in which it is shown by the aid of first-principles electronic structure calculations that the small Ce magnetic moment on CeMn_2Ge_2 occurs due to an almost total cancellation of its spin and orbital contributions whereas the same cancellation does not occur with the MHF. Although the results of the electronic structure calculations presented in Ref. [4] reproduced the expected magnetic properties of the CeMn_2Ge_2 compound like the small Ce magnetic moment, the known Mn(3d)–Ce(5d) hybridization scheme and the experimental Ce valence, it failed to reproduce the experimental MHF. The reason for the discrepancy was attributed to the failure of the local-density-approximation

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(LDA) with its generalized-gradient-approximation (GGA) version employed within the density-functional theory (DFT). Within this approach, the Ce 4f states are treated as ordinary Bloch states and thus it neglects the correlation effects that tend to localize them. It is well known that as a consequence all the Ce 4f spectrum appears pinned at the Fermi level in the electronic density of states as well as a probably incorrect Ce 4f ground state is formed since it is composed just of an average on its $L = 3$ orbitals.

The aim in the present work is to study the effects produced on MHF on Ce atoms in CeMn_2Ge_2 in the case where their 4f electrons are treated as localized electrons within the GGA + U approximation. Since the Ce MHF and especially its orbital component is very sensitive to the way the 4f orbitals are populated, it can serve as a guide to search for a correct electronic ground state of Ce atoms in CeMn_2Ge_2 .

2. Electronic structure calculations

Electronic structure calculations are a useful tool in the interpretation of MHF data since they can give us information on the several components of the MHF as well as on the related electronic states of the atoms under study. The aim in the present study on the CeMn_2Ge_2 compound is to find the orbital, dipolar and the Fermi-contact contributions to the MHF acting on cerium atoms, compare the result with the experiment and to determine the corresponding ground state of the Ce 4f electronic shell structure.

The theoretical basis behind these calculations is the DFT in which all the relevant observables are represented as a functional of the electronic density. The great advantage of this method is that the complex many-particles problem of the electronic system of an ensemble of atoms can be treated as a problem of noninteracting particles [5]. The ground state of the electronic system is determined by finding the spin densities that minimize the total energy given by:

$$E[\rho] = T_s[\rho] + E_{\text{ei}}[\rho] + E_{\text{H}}[\rho] + E_{\text{ii}}[\rho] + E_{\text{xc}}[\rho]. \quad (1)$$

Here, ρ denotes the spin densities $[\rho] \equiv [\rho \uparrow, \rho \downarrow]$. The terms in this expression represent, respectively, the single particle kinetic energy, the Coulomb interaction between electrons and nuclei, the Hartree component of the electron–electron interaction, the interaction between atomic nuclei and the exchange–correlation energy. Usually the exchange and correlation energy is treated by the LDA, which simulates, locally, the respective energies of a uniform electron gas. This approximation fails to describe the large correlation effects that are present, for instance, within the 4f electronic shell of the rare-earths, even when the improved GGA [6] is employed.

An alternative approach that significantly improves on the description of correlated electronic systems in comparison with the LDA/GGA is the LDA/GGA + U (generically known as DFT + U) where an extra term is added to

the hamiltonian that take into account the intra-shell Coulomb and exchange interactions [7]:

$$H = \frac{U}{2} \sum_{m,m',\sigma} n_{m\sigma} n_{m'-\sigma} + \frac{U-J}{2} \sum_{m \neq m',\sigma} n_{m\sigma} n_{m'\sigma}, \quad (2)$$

where $n_{m\sigma}$ is the operator yielding the occupation number of an orbital with magnetic quantum number m and spin σ , U describes the energy required for adding an extra electron to the shell and J represents the exchange energy. The DFT + U energy is obtained by subtracting the contributions already existing in the DFT (double-counting):

$$E_{\text{DFT}+U} = E_{\text{DFT}} + \frac{U-J}{2} \sum_{m\sigma} (n_{m\sigma} - n_{m\sigma}^2). \quad (3)$$

An effective energy parameter $U_{\text{eff}} = U - J$ is therefore defined. Unfortunately, in this case, the value of U_{eff} cannot be obtained through the variational principle. It has to be known a priori for a specific compound or must be determined in a way that a measured parameter fits with the calculated one, as was done in the present work.

To minimize the energy expressed in Eq. (1), a system of Kohn–Sham single-particle equations has to be solved, numerically, in a self-consistent way. For this purpose, a set of basis functions has to be defined. A specially adapted basis set of functions that allows a very precise description of electronic density at the nuclear position, well suited to study hyperfine fields, is utilized in this work. Basically it consists of a linear combination of radial functions multiplied by spherical harmonics inside nontouching spheres centered at the atomic positions and plane-waves at the interstitial space that matches appropriately the functions inside the spheres on the surface. Details of this Augmented plane waves plus local orbitals (APW + lo) methodology is given in the WIEN2k computer package documentation [8].

The spin–orbit interaction was taken into account by employing a second variational method. The plane-wave basis was limited to $K_{\text{max}} = 8/R_{\text{MT}}$ where the smaller muffin-tin radius is $R_{\text{MT}} = 2.2 \text{ \AA}$. For Brillouin zone integration, a tetrahedral mesh of 2500 points was utilized. For the lattice parameters the experimental values determined at 12 K were used: $a = 4.129 \text{ \AA}$, $c/a = 2.640$, and the position parameter of the Ge atoms inside the cell is $z = 0.382$ [9].

3. Results

The Ce ions in CeMn_2Ge_2 are located in a site with tetragonal point symmetry 4/mmm. As a result its ${}^2F_{5/2}$ states are expected to be split by the crystalline field according to the following wave functions [10]:

$$\begin{aligned} \Gamma_7^1 &= \alpha \left| \pm \frac{5}{2} \right\rangle - \beta \left| \mp \frac{3}{2} \right\rangle, & \Gamma_7^2 &= \beta \left| \pm \frac{5}{2} \right\rangle + \alpha \left| \mp \frac{3}{2} \right\rangle, \\ \Gamma_6 &= \left| \pm \frac{1}{2} \right\rangle. \end{aligned} \quad (4)$$

As stated before, the GGA + U methodology no longer satisfies the variational principle and a self-consistent-field (scf) solution usually converges to an electronic state that intimately resembles the state at the start of the scf cycle. We take this as an advantage and determined a converged electronic structure of CeMn_2Ge_2 for each of the Ce 4f states given in Eq. (4). For these calculations we adopted $U_{\text{eff}} = 0.55 \text{ Ry}$ which is the same as for metallic Ce taken from Ref. [11]. The resulting Ce MHF contributions along with the total energy are shown in Table 1.

The sign of the Ce MHF was not determined experimentally [3] and thus we will compare only the magnitude. In comparing the values of the MHF we keep in mind that the greatest expected disagreement would be for the case of the Fermi-contact field, which can be as large as 30% [12]. The orbital and dipolar contributions, which depend only on the angular momentum projection L_z and the $\langle I/r^3 \rangle$ operators are expected to give much more reliable values from the calculations.

From Table 1, $U_{\text{eff}} = 0.55 \text{ Ry}$, it can be seen that the total Ce MHF does not agree with experiment ($39.0 \pm 1.4 \text{ T}$) for any of the Ce 4f ground states. The difference is +34% for the Γ_6 and -33% for Γ_7 states, respectively. In the case of the GGA calculations, the resulting total MHF value was -15.7 T, a much worse agreement with experiment than the present GGA + U calculations. The effect caused on the MHF as the localization of the Ce 4f electrons is taken into effect within GGA + U , can be noticed however, in comparison with GGA: The magnitude of the MHF increased from 15.7 to until 51.7 T. This observation raised the question as to whether our present calculations tend to localize the electrons too much and if the result can be tuned by an appropriate value of the parameter U_{eff} .

In Fig. 1 is shown the variation of the total Ce MHF as a function of U_{eff} for the Γ_6 and Γ_7^2 Ce 4f states. The magnitude of the MHF increases as a function of U_{eff} and crosses the experimental value at $U_{\text{eff}} \sim 0.13 \text{ Ry}$ when the Ce state is Γ_6 . The same trend is verified for the Γ_7 states but in these cases the magnitude of MHF does not attain the experimental value.

In Table 1 is also shown the resulting MHF values for the $U_{\text{eff}} = 0.13 \text{ Ry}$ case in the last three columns. As

expected, the agreement of the MHF value from the Γ_6 state with experiment is remarkable. Also shown is that the Γ_7 states depart from the experimental value mainly due to the dipolar contribution which is relatively large for Γ_6 in comparison with the corresponding values for the Γ_7 states. The Fermi-contact contribution remains quite constant for all the cases, including the GGA case.

A question that arises now is if the Γ_6 state is physically reliable as the Ce ground state in CeMn_2Ge_2 , since, as can be seen also in Table 1, the Γ_7 states present a lower energy relative to the Γ_6 state according to the GGA + U calculations. A known argument that favors the assignment of Γ_6 as a ground state is that we usually can no longer compare energies within the GGA + U methodology since the variational principle is not satisfied.

However, better arguments can be realized. It is known that CeMn_2Ge_2 is a Kondo system with $T_K = 18 \text{ K}$ [3] and a crystalline-field splitting energy $T_{\text{CF}} \sim 56 \text{ K}$ is estimated from the transition seen in the Ce MHF curve as a function of temperature [3]. In this case, the condition $T_K < T_{\text{CF}}$ is satisfied, then imposing that only Γ_6 state operates at low temperatures [13]. The present work thus provides additional evidence since only the Γ_6 state can reproduce the experimental MHF in present GGA + U calculations.

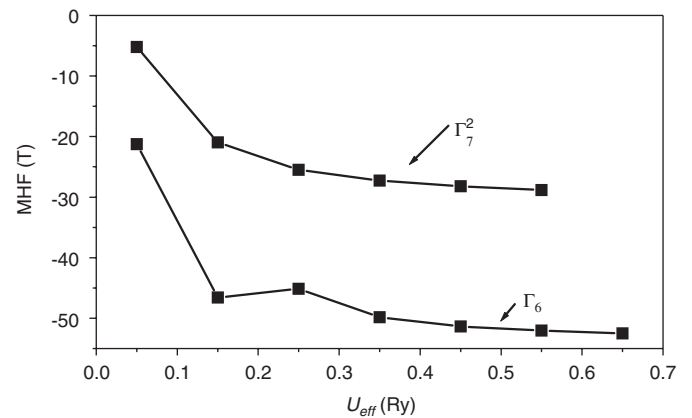


Fig. 1. Variation of the total MHF as a function of the parameter U_{eff} for each of the Ce ground states Γ_6 and Γ_7 .

Table 1

Contributions to the magnetic hyperfine field acting on Ce ions in CeMn_2Ge_2 for the three possible Ce 4f ground states resulting from GGA + U calculations

	$U_{\text{eff}} = 0.55 \text{ Ry}$			$U_{\text{eff}} = 0.13 \text{ Ry}$		
	Γ_6	Γ_7^1	Γ_7^2	Γ_6	Γ_7^1	Γ_7^2
Contact	15.1	14.3	14.3	14.5	14.0	13.9
Dipolar	-14.2	-0.215	0.323	-12.0	-0.369	0.377
Orbital	-52.6	-39.1	-41.7	-44.4	-34.5	-33.9
Total	-51.7	-25.0	-27.1	-41.9	-20.9	-19.6
Energy	-0.8452	-0.8517	-0.8529	-0.8828	-0.8857	-0.8913

Values in T and the signals are relative to the Mn magnetic moment $\mu_{\text{Mn}} = -2.3\mu_B$. Experimental MHF at 10 K = $39.0 \pm 1.4 \text{ T}$ (Only the magnitude is known). Total energy is relative to -30761 Ry.

4. Conclusion

By applying a methodology in $GGA + U$ calculations in which crystal-field wave-functions are tested individually and choosing the Hubbard-like parameter U_{eff} in order that the resulting MHF matches with the experimental value, we were able to propose the Γ_6 Ce state as the ground state in CeMn_2Ge_2 . This state however presents a higher total energy in comparison with the Γ_7 states according to the $GGA + U$ results. Since CeMn_2Ge_2 is known to present Kondo physics at low temperatures satisfying the $T_K < T_{\text{CF}}$ relations, it enforces the Γ_6 assignment as the ground state.

Acknowledgements

Partial support for this research was provided by the Fundação de Amparo à Pesquisa do Estado de São Paulo. JMF expresses his sincere thanks to Prof. Peter Blaha from Vienna University of Technology and to Dr. Pavel Novák from the Academy of Sciences of the Czech Republic for their kind assistance in the DFT + U method.

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