Study of Ce intermetallic compounds: an LDA classification and hybridization effects

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Abstract

Spin-polarized calculations within the LDA approximation have been done with the goal of characterizing Ce intermetallic compounds. Symmetry and chemical environment effects on 4f hybridization and, thereafter, on magnetization effects have been studied.

I. INTRODUCTION

In the last decades, Ce intermetallic compounds have received a lot of attention both in theory and experiment. On one side, these systems can exhibit a large variety of behaviors, such as superconductivity, huge magnetoresistance, itinerant magnetism, etc. On the other side, the nature of the 4f states is controversial since it has not been established yet which systems can be treated using a bandlike picture and which ones using a localized one. In the first picture, the effective electronic correlation is weak and the 4f states form a narrow band, while in the second one, the 4f electrons are highly correlated and interact weakly with the conduction band.

The main difference between Ce and other rare earth systems is that, in the case of Ce, the 4f state is energetically very close to the Fermi level so that its occupation number and the strength of hybridization with the conduction electron bands strongly depend on the chemical and geometrical environment. In that sense, we can understand the complexity of the phase diagram of pure metallic Ce which, depending on temperature and pressure, can be magnetic, paramagnetic or superconducting. Due to this fact, different types of magnetism have been observed within the intermetallic compounds: intermediate valence behavior, Kondo effect and magnetic ordered structures (FM, AF) are among them. Intermediate valence behavior appears in systems having the states with n and n – 1 4f electrons almost degenerate. The nearly degenerate condition is a consequence of hybridization of the 4f states and results in a configuration with a non integer electronic occupation number $n_{4f}$. In general, intermediate valence materials show anomalous values for some physical properties such as lattice parameter, bulk modulus, magnetic susceptibility, etc, as compared to systems
with an integer $4f$ occupation number. The intermediate valence behavior in $Ce$ compounds is characterized by having a very small or zero magnetic moment.

The different physical situations posed by these systems have been traditionally described by many body hamiltonians which consider strong electron-electron interactions and treat hybridization as a small perturbation. Kondo systems, for which correlations are dominant, have to be treated with these model hamiltonians. In $Ce$ intermetallics, particularly, it is not clear at all how important the relative strength of hybridization and correlations are. There are systems whose electronic ground state can be well described by an itinerant picture, namely those in which $4f$ hybridization plays a relevant role giving rise to a decrease in correlation effects.

In this work our aim is twofold. First we want to use the band picture to establish a criterion for characterizing the ground state of $Ce$ intermetallic compounds by analysing their LDA spin contribution to the magnetic moment. As a second goal, and using for this the established criterion as a tool, we also want to analyse the dependence of the magnetism of $Ce$ on geometrical and chemical environment. For this we study a variety of $Ce$ compounds, whose magnetic properties are experimentally well known. We claim that it is possible to determine to which regime the system under study belongs. That is, if we are dealing with strongly hybridized or strongly localized systems, going through the intermediate situations, by analysing the itinerant magnetic contribution that results from spin polarized LDA calculations. This analysis is certainly done in the knowledge that only those $Ce$ compounds whose $4f$ states are essentially itinerant can be well described within the LDA band theory frame. Actually, a proper treatment for the $4f$ electrons would be to include the self-interaction correction (SIC) in the calculations but this is not necessary for the kind of description undertaken in this work.

Once we have established our characterization tool, we discuss the relative importance of chemical and crystalline environment on hybridization and thereafter on the determination of the magnetic state of intermetallic systems of the type $CeX_n$ with $n$ equal or larger than one.

This paper is organized as follows. In Sec. II we report the results of calculations done for several real systems and present a discussion of how the LDA approximation can be used to classify them into magnetic, intermediate valence or paramagnetic compounds. In the second part of this section we analyse the influence of chemical and structural environment on the magnetic ground state of $Ce$ compounds. We finally present the conclusions in Sec. III.

II. ELECTRONIC STRUCTURE CALCULATIONS

In this work we perform ab-initio calculations using the Full Potential Linearized Augmented Plane Waves (FP-LAPW) method in the Local Density Approximation (LDA). We use the exchange and correlation potential of J.P. Perdew and Y. Wang. We make both paramagnetic and spin polarized calculations. The sampling of the Brillouin zone used to calculate the electronic ground state depends on the size and symmetry of each system. In general, from 800 to 1400 k-points in the first Brillouin zone are enough for convergence. The considered muffin tin radii, $R_{mt}$, are equal to 2.8 au for Ce, 2.4 au for 4$d$ transition metals (TM), 2.0 au for 3$d$ transition metals (TM), 1.8 au for S and 1.6 au for N.
cutoff parameter which gives the number of plane waves in the interstitial region is taken as $R_{mt}K_{max} = 8$, where $K_{max}$ is the maximum value of the reciprocal lattice vector used in the expansion of plane waves in that zone. The total energy is converged up to $10^{-4}Ry$.

A. Characterization of Ce compounds through their LDA magnetic moments

It is well known that Ce has one 4$f$ electron in the solid. As we have mentioned before, the energy of this 4$f$ state is very close to the Fermi level so that it is, in principle, very sensitive to chemical and geometrical environment. In some compounds Ce keeps its magnetic moment equal to $1 \mu_B$ and in others it can decrease even going to zero. In this Section we establish a way of characterizing Ce compounds which allows us to classify them into magnetic, intermediate valence or paramagnetic by doing LDA spin polarized calculations. To achieve this we study compounds whose magnetic properties have already been reported and are listed in Table I.

$CeNi$, $CeRh$ and $CePd_3$ are accepted to be intermediate valence compounds while $CeN$ and $CeRh_3$ are well described by an itinerant picture, being paramagnetic. $CeS$, $CePd$, $CeAg$ and $CeCd$ are magnetically ordered systems. Table I contains the structural data and the experimental ordering temperatures, $T_C$ and $T_N$, which correspond to the Curie and Nèl temperatures depending on whether the compounds are ferromagnetic or antiferromagnetic. No magnetic order has been experimentally observed for the cases where no ordering temperature is shown.

In our calculations three types of magnetic configurations are possible: paramagnetic (P), ferromagnetic (F) and antiferromagnetic(AF). In Table I we also list the more stable configuration and the obtained LDA magnetic moment of Ce for the different compounds. The calculations are performed at the experimental volumes shown in the same table.

The obtained magnetic moments for the compounds $CeNi$, $CeRh$ and $CePd_3$ are far from being $1\mu_B$ but they are clearly not zero so that we cannot consider them as being paramagnetic. In that sense it is not surprising that these compounds are those which are widely accepted to be intermediate valence systems. An intermediate valence system is usually defined in the literature as one having in the average a non integer number of 4$f$ electrons.

It is very important to keep in mind that LDA calculations cannot account for the strong correlation effects that may occur in some rare earth compounds. However, we can infer from their itinerant contribution and using LDA the correct ground state for the systems studied here.

Based on the comparison of experimental data and our LDA results, we propose that, depending on the LDA magnetic moment, a Ce compound can be considered as

- Itinerant if $\mu_{Ce} = 0$,
- Intermediate valence or $\mu_{Ce} < 0.5\mu_B$,
- Magnetic if $\mu_{Ce} > 0.5\mu_B$.
The systems that are accepted to be itinerant, such as CeN and CeRh$_3$, are the ones whose magnetic moment is exactly equal to zero. That is, when in a given Ce system the magnetic moment is zero the 4f electrons have a strong itinerant character.

In Ce compounds the degree of localization is closely related to the strength of Ce hybridization and consequently to the magnetic state. Let us take two extreme situations as examples, CeRh$_3$ and CeAg. In Figure 1 we show an electronic charge density plot corresponding to one of the Kohn-Sham orbitals with energy close to the Fermi level and with 90% of 4f character. In the CeRh$_3$ case, there is a mixing between Rh and Ce states near $E_F$ while, this is not the case for CeAg, as can be clearly seen in Figure 1.

We can also analyse the degree of hybridization by comparing 4f and 4d partial densities of states (Figure 2). The most striking difference between CeRh$_3$ and CeAg systems is that in the last one, the 4d and 4f bands are approximately 4 eV apart being both of them very narrow, of the order of 1eV, while in CeRh$_3$, the 4d band is more extended in energy (about 4eV), leading to an energy region around the Fermi level where hybridization is important. Thus, taking into account the calculated magnetic moments and using the established criterion, we say that in the compound where the 4f band is more hybridized, namely CeRh$_3$, the 4f band turns more delocalized leading thus to a non magnetic Ce. This should hold in general.

B. Dependence of Ce magnetism on crystalline and chemical environment

Ce can completely or partially loose its magnetic moment depending on chemical and crystalline environment. In this section we study how 4f hybridization affects the Ce magnetic moment depending on the local symmetry and the chemistry of the ligand. The 4f band hybridizes not only with 4f electrons of neighboring Ce sites but also with orbitals of the ligand (4d, 3d or sp bands). Both types of hybridization produce a decrease in the magnetic moment of Ce.

For the symmetry considerations, we compare systems of the type CeX (X=Ni, Rh, Pd) and analyse them in the CrB and CsCl crystal structures. These structures are being taken as prototypes of different symmetries within the same relative composition. Actually, both structures appear in nature associated with CeX compounds. In general, when X is a latter TM the observed structure is CrB and when X belongs to the 1B, 2B or the 3A column of the periodic table the corresponding structure is the CsCl one.

The calculation for a given CeX system in both the CrB and the CsCl structures helps us to understand how local symmetry affects 4f hybridization and consequently the magnetization of Ce. The calculations within the CrB structure are performed at the experimental equilibrium volume at room temperature and, since the CsCl structures are hypothetical ones for CeNi, CeRh and CePd, we take the same volume per atom as in CrB in order to be able to compare the outcoming magnetic properties.

From Table II we see that the CsCl structure favours magnetism, even if slightly, as compared to the CrB one. This is a consequence of CsCl having higher symmetry. Crystal field effects lead, in the CrB case, to a lifting of almost all of the 4f degeneracies while this is not the case in the CsCl structure. Within a ‘quasi’-Stoner image CsCl favours magnetism due to a higher density of states at the Fermi level. This is coherent with the fact that only some of the CrB compounds are magnetic while all of the CsCl ones are magnetic.
Figure 3 shows charge density plots with contributions stemming from the energy range $0.7E_F < E < E_F$, where $E_F$ is the Fermi energy. In this range the 4f band is the most important one. The plots show, for the CeRh system, the charge densities projected into the (010) plane for CrB and into the (110) one for CsCl. In the CrB structure the 4f-4f hybridization between neighboring Ce sites is more important than the 4f-4d or 4f-3d hybridization between Ce and TM atoms. This can be inferred from the fact that there is more charge between Ce atoms than between Ce and TM, namely a weight of 0.02 in CrB as compared to 0.007 in CsCl. On the other hand, the 4f-d hybridization is stronger in CsCl than in CrB. The amount of total interstitial charge is practically the same in both structures: CrB and CsCl structures have 4.4 and 4.3 interstitial electrons per formula unit respectively. The difference among them comes from the spatial distribution of charge.

For the systems under study which crystallize in the CsCl structure, symmetry makes a contribution to the magnetic moment of Ce, but it is actually not the crystalline environment the determining factor for the magnetic behavior. It is rather the chemical nature of the ligands the one that is responsible for this magnetic result. Considering for instance, the CeAg or CeCd system from the previous section, which crystallize in the CsCl structure, the 4d band lies very low in energy and thereafter there is nearly no hybridization between 4f-4d bands, leading this to the magnetization of Ce. In the hypothetical situation that one could force these systems to crystallize in the CrB structure they would also be magnetic.

On the other hand, if we compare the magnetization of CeNi, CeRh and CePd focusing on the CrB structure, which is the real one for these compounds, we can get insight into the effect that the type of ligand has on the magnetic moment of Ce. Using our criterion CePd is a magnetically ordered system, while CeRh and CeNi are not when considered in their natural CrB structure. In Figure 4 we show the densities of states for the three compounds. The different magnetic solutions within the same crystalline structure can be explained, by the fact that in CeRh the 4d band is closer in energy to the Fermi level than in the Pd compound and consequently 4f-4d hybridization is stronger. The more the 4f band hybridizes with the 4d band the smaller is the Ce magnetic moment. On the other hand, in the CeNi case, there is an interplay between two types of hybridization namely Ce-Ce and Ce-Ni, both induce a decrease of the magnetism of Ce as compared to CePd. Actually, in CeNi, there is a reduction in volume and Ce atoms are nearer to each other than in CePd. Consequently, as can be seen from the densities of states in Figure 4, the 4f band is 0.5 eV wider in CeNi than in CePd due to an increase in Ce-Ce mixing. On the other side, the 3d band lies nearer to $E_F$ than the 4d one this giving rise to 4f-3d mixing. Due to this interplay CeNi is the less magnetic compound among the CrB systems.

III. CONCLUSIONS

In this contribution using an itinerant picture we show that it is possible to characterize the magnetic ground state of Ce intermetallic compounds by doing ab-initio calculations within the LDA approximation. This criterion allows us to classify them into magnetically ordered, intermediate valence or paramagnetic systems through their calculated spin contributions to the Ce magnetic moment. It is based on the band theory frame in which, in general, correlated Ce systems are not well described. However we find that it is an useful tool to obtain qualitative information about the electronic ground state of a wide variety
of $Ce$ compounds, including those with strong electronic correlations.

We study the importance of $4f$ hybridization in determining the magnetic state of $Ce$ by analysing both symmetry and chemical effects. We study first the influence of the symmetry environment on $4f$ hybridization in $CeNi$, $CeRh$ and $CePd$ and take CsCl and CrB as prototypes of high and low symmetry structures. We see that CsCl slightly favour magnetism as compared to CrB. This fact can be understood with the following argument: CrB’s local environment has less symmetry operations than CsCl (8 vs. 48) and consequently there is a lifting of $4f$ degeneracies giving rise to a smaller density of states at the Fermi energy. Within a Stoner picture there is a stronger instability for magnetism in CsCl than in CrB. In this sense we can understand the fact that all the systems with the formula unit CeX are magnetic when growing in the CsCl structure (with X belonging to the 1B, 2B and 3A column of the periodic table) but they are not when growing in the CrB, in which only $CePd$ and $CePt$ are magnetically ordered.

Noteworthy is the fact that, in the cases studied, local symmetry is not a determining factor for the magnetic behavior. It is actually the type of ligand the crucial factor to determine the magnetic state. Along this line, we focus our study on the CrB structure to analyse the effect of chemical environment. We conclude that both $4f$-$d$ and $4f$-$4f$ types of hybridization can lead to a decrease of $Ce$ magnetic moment in the systems $CeRh$ and $CeNi$ with respect to $CePd$. In the first case it is mainly the mixing between the $4d$ band of $Rh$ with the $4f$ one from $Ce$ what produces a strong decrease in the magnetic moment. In the second case, $CeNi$, both types of hybridization occur, resulting this in an even lower value of the magnetic moment of $Ce$.

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| Compound | Crystal structure | $a$ (Å) | $b$ (Å) | $c$ (Å) | $T_C$ (K) | ground state | $\mu_{Ce}(\mu_B)$ |
|----------|------------------|---------|---------|---------|-----------|-------------|-----------------|
| CeN      | NaCl             | 5.02    | -       | -       | -         | P           | 0               |
| CeS      | NaCl             | 5.79    | -       | -       | 8.3$^*$   | AF          | 0.61            |
| CeNi     | CrB              | 3.78    | 10.37   | 4.29    | -         | int.val.    | 0.26            |
| CeRh     | CrB              | 3.85    | 10.98   | 4.15    | -         | int.val.    | 0.42            |
| CePd     | CrB              | 3.89    | 10.91   | 4.63    | 6.6       | F           | 0.83            |
| CeAg     | CsCl             | 3.76    | -       | 9       | F         | P           | 0.88            |
| CeCd     | CsCl             | 3.86    | -       | 16.5    | F         | P           | 1.01            |
| CeRh$_3$ | AuCu$_3$         | 4.02    | -       | -       | P         | F           | 0.83            |
| CePd$_3$ | AuCu$_3$         | 4.12    | -       | -       | int.val.  |             | 0.22            |

TABLE I. Structural data, ordering temperatures, magnetic ground state and calculated magnetic moment of $Ce$ for some compounds. Those systems where there is no value for $T_C$ do not present magnetic order. * indicates antiferromagnetic order. P: paramagnetic. AF: antiferromagnetic order. F: ferromagnetic order.

| Compound | V($\text{Å}^3$) | $\mu_{Ce}(\mu_B)$ |
|----------|-----------------|--------------------|
| CeNi     | 21.02           | 0.26               |
|          | 21.02           | 0.48               |
| CeRh     | 21.93           | 0.42               |
|          | 21.93           | 0.55               |
| CePd     | 24.56           | 0.83               |
|          | 24.56           | 0.86               |

TABLE II. $Ce$ magnetic moment in $CeNi$, $CeRh$ and $CePd$ systems in both CrB and CsCl crystal structures at the same volume per atom in the unit cell.
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FIGURES

FIG. 1. Charge density plots corresponding to a Kohn-Sham orbital associated with an eigenvalue close to the Fermi energy in which the 4f character is the most relevant. These densities are projected into the plane (110) for the system CeAg (above) and into the (100) one for the system CeRh$_3$ (below).

FIG. 2. 4d and 4f partial densities of state of CeAg and CeRh$_3$ obtained from paramagnetic calculations. The zero level corresponds to the Fermi energy.

FIG. 3. Charge density plots for the system CeRh in both CrB and CsCl crystalline structures. Charge density contributions coming from the energy range $0.7E_F < E < E_F$ , in which the 4f band is more important, are plotted. Above: charge densities projected into the (010) plane of the CrB crystal structure. Below: Charge densities projected into the (110) plane of the CsCl crystal structure.

FIG. 4. 4d and 4f partial densities of states of CeNi, CeRh and CePd obtained from paramagnetic calculations. The zero level corresponds to the Fermi energy.
