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Influence of $4f$ hybridization on the structural and electronic properties of CeM_2Si$_2$ (M=Ru, Rh, and Pd)

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We present full potential *ab initio* calculations to study structural and electronic properties of CeM_2Si$_2$ with M=Ru, Rh, and Pd. Two kind of calculations are performed: one considering the $4f$ states as hybridized ones and another simulating Ce systems with nonhybridized $4f$ states. We calculate the hybridization function and analyze the influence of the $4f$ states on structural properties such as equilibrium volume, c/a ratio, and *bulk modulus* and study their evolution together with that of the spin magnetic moment under applied hydrostatic pressure. The results are compared with experimental data.

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I. INTRODUCTION

Cerium compounds present several unusual physical properties, which have their origin in the behavior of the highly correlated $4f$ electrons. The hybridization of the $4f$ states with the conduction band is considered as the parameter that controls the wide variety of ground states observed in these systems. Hybridization can be tuned in two ways: by applying hydrostatic pressure or by changing the chemical environment of Ce. In particular, the family of CeM_2X_2 intermetallics (with M a transition metal and X a p-type metalloid) which crystallizes in the ThCr$_2$Si$_2$-type structure shows a wide variety of physical behaviors depending on M and X, such as ambient or pressure induced superconductivity, long-range magnetic order, heavy fermion character, paramagnetism, and nonmagnetic order with magnetic correlations, among others.[1]

The competition between the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and the Kondo effect determines the ground state of these systems. In a regime of weak hybridization the dominant RKKY interaction leads to long-range magnetic order, while in the case of strong hybridization the Kondo interaction prevails and spin compensation favors a nonmagnetic valence fluctuating state at low temperatures.[2]

Within the above-mentioned family of compounds, our interest lies on the study of the influence of $4f$ and conduction-band hybridization on the structural and electronic properties of the CeM_2Si$_2$ series, being M a $4d$ transition metal with increasing d-occupation number (M=Ru, Rh, and Pd).

The low-temperature properties of these systems can be briefly summarized as follows. CeRu$_2$Si$_2$ is a heavy fermion and its low-temperature behavior is well described as a paramagnetic Fermi liquid, in which no long-range magnetic order has been observed down to 20 mK. The low-energy excitations are strongly renormalized heavy quasiparticles, as inferred from the large value of its specific-heat coefficient γ.[3]

CePd$_2$Si$_2$ and CeRh$_2$Si$_2$ show antiferromagnetic order (AF) being their respective Néel temperatures $T_N\sim 10$ K and 36 K. Both systems show a rather fast decrease in the value of T_N with applied pressure, which is the prelude of pressure induced superconductivity in both cases. In CePd$_2$Si$_2$ the critical pressure at which AF is suppressed was reported at $P_C\sim 2.5$ GPa, while for CeRh$_2$Si$_2$ a lower $P_C\sim 0.9$ GPa destroys the AF order.[4]

Among the peculiarities shown by the systems under study, there is a controversy about the nature of the $4f$ states in CeRh$_2$Si$_2$, on the one hand, the fact that CeRh$_2$Si$_2$ has a large ordering temperature and that the value of the magnetic moment of Ce is close to the free-ion one ($\mu_{ord}=1.5\ \mu_B$) (Ref. 5) suggests that the $4f$ states are very localized in this compound. On the other hand, the evolution of these quantities with applied pressure and the large value of the Kondo temperature ($T_K \approx T_N$) as compared to other compounds of the CeM_2Si$_2$ family, leads to the assumption that the $4f$ states are strongly hybridized and quite delocalized.[6] Another peculiar feature of CeRh$_2$Si$_2$, which makes out of it a singular system in the series, is the anomalous value of its lattice parameters, showing the highest c/a value within the series.

With the aim of getting deeper insight into the different kinds of behaviors observed in this family of compounds, several experiments have been recently done to follow the evolution of the c/a ratio and of the cell volume as a function of chemical substitution and also to study their relationship with magnetic, thermal, and transport properties.[7,8] For instance, it has been reported that a decrease in the concentration of Rh in the alloy Ce(Ru$_{1-x}$Rh$_x$)$_2$Si$_2$ induces the same effect as the application of pressure for the compound with $x=0.05$. That is, under these two control parameters a reduction of the c/a value and in the Ce-Ru distances take place. This seems to play a relevant role in the observed spin-density wave transition shown by this system.[9] Several experimental studies on the variation of the lattice parameters upon alloying have already been undertaken[8,10] however, as far as we are aware of, their evolution under hydrostatic pressure has not been reported yet, neither experimentally nor theoretically. This kind of results, which are difficult to obtain experimentally, are of interest in order to understand the interplay between RKKY and Kondo interactions through the analysis of the evolution of the Ce-M distances and c/a values, since the main contribution to the screening of the $4f$ comes from the transition metal. It is known that a reduction of these distances favors the Kondo interaction while the RKKY one prevails if they increase.[11]

In this contribution we address precisely to the evolution of the structure of the above-mentioned systems with hydrostatic pressure and undertake a comparative study of their properties setting particular emphasis on the influence of $4f$ hybridization. With that purpose we do systematic *ab initio* calculations for the compounds under study. Within the approximations used for the exchange and correlation potential, this kind of calculations are not able to describe the low-temperature properties of these highly correlated compounds as the many-body and correlation effects are being underestimated and statically treated. Notwithstanding this, it is possible to obtain detailed information about the ground-state electronic structure, which plays an important role in the determination of the structural properties and underlies the specific low-energy excitation spectra, through the characteristics of their respective hybridization functions. In order to study the role played by the $4f$ states on these properties we also perform calculations for the corresponding LaM_2Si$_2$ systems, which do not show occupied $4f$ states. The results are compared with available experimental data. Finally, in order to give a more quantitative answer to the $4f$-conduction-band hybridization we calculate the hybridization function itself and discuss to which extent this quantity is related to the observed behaviors in terms of Ce-M distances and $4d$ band filling.

The present paper is organized as follows. In Sec. II we describe the applied technique and the details of the calculation, in Sec. III we analyze some structural properties at equilibrium, in Sec. IV we follow the evolution with pressure of c/a, Ce-M distances and of the spin magnetic moment of Ce for the different systems under study. In Sec. V, we present the results obtained through the calculation of the hybridization function and finally, in Sec. VI we summarize and discuss our results.

II. METHOD OF CALCULATION

We perform *ab initio* calculations using the full potential linearized augmented plane-wave method (LAPW),[12] which means that no shape approximation for the potential and for the charge density are introduced. We use the exchange and correlation potential in the generalized gradient approximation (GGA) of Perdew and Wang[13] and compare with results obtained within the local-density approximation (LDA). 1000 k points are used to sample the whole Brillouin zone, with 99 k points in the irreducible one. The considered *muffin-tin* radii, R_{mt}, are taken equal to 2.6 a.u. for Ce and La, 2.2 a.u. for the $4d$ transition metals, and 2.0 a.u. for Si. For the cutoff parameter that gives the number of plane waves in the interstitial region we take $R_{mt}K_{max}=8$, where K_{max} is the largest reciprocal-lattice vector used in the expansion of plane waves in that region. The used cutoff implies 120 plane waves per atom approximately. The total energy is converged up to 10^{-4} Ry.

TABLE I. Structural properties of CeM_2Si$_2$. The second column shows the equilibrium properties obtained from calculations considering the $4f$ states as part of the valence band. The third column corresponds to the optimized values for La$_2M_2$Si$_2$, which simulate nonhybridized $4f$ systems.

CeRu$_2$Si$_2$	Experiments	$4f$ in valence	LaRu$_2$Si$_2$
Equilibrium volume	172.4 [a]	172.3	175.3
$\frac{c}{a}$	2.335 [a]	2.322	2.380
B(GPa)	105 [b]	113	103
CeRh$_2$Si$_2$			LaRh$_2$Si$_2$
Equilibrium volume	170.2 [c]	171.2	176.3
$\frac{c}{a}$	2.489 [c]	2.473	2.476
B(GPa)		104	102
CePd$_2$Si$_2$			LaPd$_2$Si$_2$
Equilibrium volume	177.4 [c]	178.9	185.2
$\frac{c}{a}$	2.331 [c]	2.354	2.330
B(GPa)		90	85

[a] Reference 14.
[b] Reference 15.
[c] Reference 16.

III. STRUCTURAL PROPERTIES

The influence of the $4f$ state on the structural properties is studied through the calculation of equilibrium volumes and c/a ratios. We additionally calculate the bulk modulus. We treat the $4f$ states as being part of the valence band and compare the results with those corresponding to LaM_2Si$_2$ compounds which have almost the same electronic structure except for the absence of $4f$ states. The calculations on the La systems provide a way of simulating a nonhybridized $4f$ state of Ce. As cohesion in metals and, thereafter, their crystal structure are mainly given by electrons in the valence bands, the equilibrium properties of those Ce compounds which have localized $4f$ electrons very often can be analyzed by making this kind of substitution. Experimentalists take advantage of this fact in order to separate the contribution of the $4f$ electrons when analyzing the thermodynamical and equilibrium properties of Ce intermetallics. In Table I we show the ground-state values of the calculated properties obtained with the above-mentioned procedures within the GGA approximation. The available experimental data are also being shown in the table.

From Table I it can be seen that the equilibrium volumes are better reproduced when the $4f$ states are considered as part of the valence band for the three systems. The calculations for LaM_2Si$_2$ give equilibrium volumes that are larger than the experimental ones for CeM_2Si$_2$. In particular, for the systems containing Rh and Pd the excess volume lies around 4% while it is around 2% for Ru. From this volume calculations we can say that, in comparison to other Ce compounds, the ones under study show an appreciable amount of 4f itineracy which cannot be disregarded when analyzing their physical properties.[16] With this statement we are certainly not meaning that the 4f states are completely itinerant, but that a certain degree of itineracy is present in the three compounds studied.

It is important to stress that the experimental trends in the evolution of the volumes with a decreasing number of 4d holes in the M atom is obtained only when the 4f states are considered as part of the valence band. The calculated equilibrium volumes of $\mathrm{Ce}M_2\mathrm{Si}_2$ go down from Ru to Rh and increase again when going over from Rh to Pd, in agreement with the experiments. In the La series the volumes grow steadily from Ru to Pd. The consideration of hybridized 4f states versus nonhybridized ones shows, then, well differentiated trends.

With respect to the c/a ratios, it can be seen that the calculated c/a value for Ru fits better with the experimental results if the 4f states are hybridized with the valence band. In the case of Rh the ratio is rather insensitive to hybridized or nonhybridized 4f states, while the system with Pd shows a better performance for this ratio when calculated with nonhybridized 4f states. But as a whole, the evolution of this ratio along the series is mainly determined by the transition-metal d-occupancy, as it can be observed when comparing with the c/a values of the La series.

The calculated bulk modulus B of $\mathrm{CeRu_2Si_2}$ is more sensitive to the presence of 4f states than in the cases of Rh and Pd, as it can be appreciated when comparing with the results of calculations done without 4f states in the valence band. Actually, it can be assured that the tendency for the evolution of B is that its value decreases as a function of increasing 4d band filling. This also happens within the 4d transition-metal series for bulk Ru, Rh, and Pd. Only the experimental data for $\mathrm{CeRu_2Si_2}$ is available in the literature, and the calculated value compares well with it. We cannot draw a conclusion on the influence of 4f hybridization from the comparison with the only one available experimental data due to errors involved both in measuring B and in its calculation.

Amid making calculations replacing Ce by La, we have also performed calculations considering the Ce 4f electron fully localized in a core level, which means that we place one electron in the 4f state and treat this state as part of the inner core.[17] The 4f electron charge is, in this way, entirely confined within the Ce *muffin-tin* region, and does not hybridize with the conduction band. Within this last approach we have calculated the equilibrium volumes and c/a ratios for $\mathrm{CeRh_2Si_2}$ and $\mathrm{CePd_2Si_2}$, obtaining similar volumes even if some differences in the c/a values when comparing with the corresponding $\mathrm{La}M_2\mathrm{Si}_2$ systems. More precisely, by taking the 4f states as core levels we obtain $V = 177$ Å^3 and $c/a = 2.502$ for the system with Rh and $V = 186$ Å^3 and $c/a = 2.346$ for Pd. As part of the above-mentioned procedure and in order to treat the 4f states as core ones, their energy has to be shifted to negative values to be handled as bound states by an atomic program. The criterium for choosing the mentioned energy shifts within LAPW has to be, naturally, the same for the three tackled systems. But this criterium is somehow arbitrary as we are introducing a parameter in an *ab initio* calculation. Thereafter, we consider that the replacement of Ce by La constitutes a more transparent way to study the influence of the 4f states on the structural properties. In spite of this, the conclusions drawn for the influence of 4f hybridization on the equilibrium volumes and for the trends of c/a coming out of this last procedure are completely in agreement with those obtained when replacing Ce by La as it was expected.

We have also performed calculations within LDA obtaining as a whole a less good agreement than within GGA. As it is usual, LDA equilibrium volumes are always reduced with respect to the experimental values and to the GGA ones, if the 4f's are considered in the valence band. On the other hand, when they are considered as core electrons the c/a values of the studied systems depart more from the experimental ones as within GGA. Taking this into account and the well-known drawbacks of LDA when calculating equilibrium properties, we present in the following sections just the results obtained within GGA.

IV. EVOLUTION UNDER HYDROSTATIC PRESSURE

In the preceding section we have seen that in the three systems under study the 4f state of Ce shows a certain degree of itineracy or hybridization with the conduction band. The degree of hybridization can be controlled through chemical or external pressure. As mentioned above, there have been extensive studies on the evolution of electronic, magnetic, and transport properties under the application of hydrostatic pressure on the $\mathrm{Ce}M_2\mathrm{Si}_2$ series and their alloys.[6,9,18] We undertake here the study of the evolution of the structural properties under hydrostatic pressure and simulate this as follows: We obtain first the equilibrium volume for a given system, the volume then is reduced stepwise as discussed in the preceding section, keeping the tetragonal symmetry of the cell and relaxing the c/a value in each step. In this way, we study the evolution of c/a and Ce-M distances with and without the 4f states in the valence band, and also the evolution of the spin magnetic moment of Ce.

A. c/a ratio and Ce-M distances

Even if there have been extensive studies of electronic, magnetic, and transport properties of $\mathrm{Ce}M_2\mathrm{Si}_2$ ($M =$ Ru, Rh, and Pd) under the application of hydrostatic pressure, no experimental results are available on the evolution of c/a and of Ce-M distances.

In Fig. 1 we show the calculated c/a ratios with pressure. Open circles, solid circles and crosses correspond to $\mathrm{CePd_2Si_2}$, $\mathrm{CeRh_2Si_2}$, and $\mathrm{CeRu_2Si_2}$, respectively. Solid lines depict the results for the corresponding La calculations which should help to disentangle the influence of 4f states on the determination of c/a. The trends of c/a are already present in the nonhybridized calculations, but the appearance of 4f hybridization remarkably enforces the tendencies (in particular, Pd and Ru cases) and there are clear differences in the role played by 4f hybridization in each case.

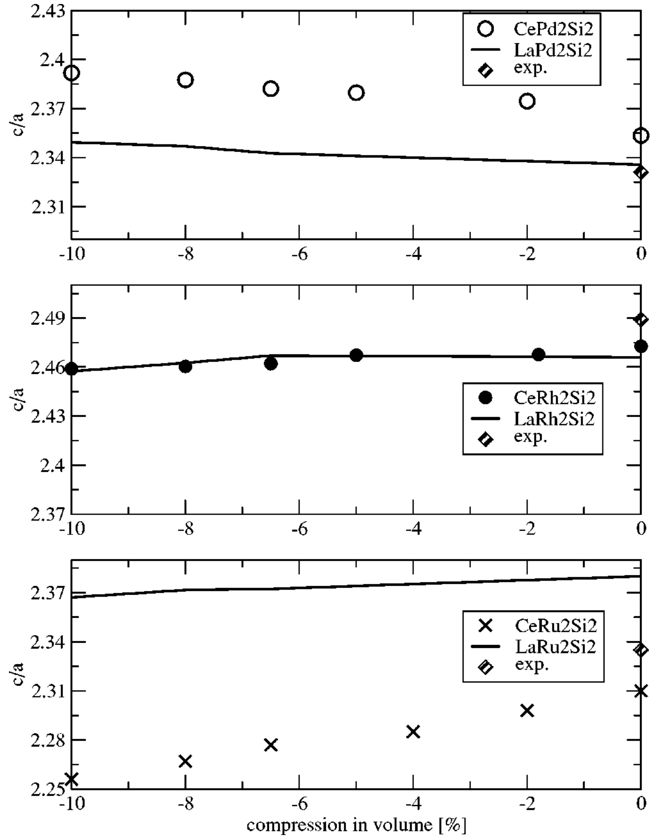

FIG. 1. Evolution of c/a with pressure.

In the system with Pd, c/a increases with applied pressure. In this case, the growing itineracy of the $4f$ states due to pressure gives rise to a slightly larger positive slope of c/a as a function of compression as compared to the situation without hybridization (La calculation). Together with the initial difference in the value of the c/a ratio between the hybridized and the nonhybridized calculation, already present at equilibrium volume, this ratio is always larger for itinerant $4f$ bands. On the other hand, in the case of Rh, c/a is not sensitive to the presence of itinerant $4f$ states nor to applied pressure. And finally, in the case of Ru, c/a decreases as a function of pressure if the $4f$'s are in the conduction band and it remains almost constant if they are not. Ru shows the largest hybridization effect on this parameter among the three systems.

The different effects of $4f$ hybridization on c/a for the three systems is a manifestation of the anisotropy of the interactions within these tetragonal compounds and depends mainly on $4f$-$4d$ hybridization. From the obtained results, that is, from the values of c/a at equilibrium volume and from the evolution of the spin magnetic moment (following section), we expect that under applied pressure the evolution of c/a will follow experimentally the behavior of the curve calculated with the $4f$ states in the valence band.

The largest value of c/a corresponds to the system with Rh, it is, namely, equal to 2.47 at equilibrium. The value of this ratio for $CePd_2Si_2$ tends to the value of $CeRh_2Si_2$, going from 2.33 to a value close to 2.4 when the cell volume is reduced. This result is consistent with the experimental behavior shown by $Ce(Pd_{1-x}Rh_x)_2Si_2$ alloys as a function of x, namely, c/a goes from 2.330 to 2.489 for x going from 0 to 1 (Ref. 8) and reflects that, in this case, both kinds of pressure, hydrostatic and chemical, lead to increasingly elongated unit cells when the volume of $CePd_2Si_2$ is being reduced until the maximum c/a is reached. Actually, when substituting Pd by Rh, there is not only a chemical pressure present but also an alloying effect due to the different number of $4d$ electrons of the involved transition metals, which leads to a larger limiting c/a value than under applied external pressure.

$CeRu_2Si_2$ is the system which presents more d holes and the repulsion among the unscreened $4d$ orbitals leads to a decrease of c/a as a function of pressure. A decreasing c/a is the mechanism which prevents Ru atoms to get closer to each other through compression. $CePd_2Si_2$, the other extreme case, is within the three compounds the one with the smallest number of d holes, the repulsion among Pd atoms is less important than in the case of Ru and this leads to an increment in the value of c/a. For hybridized $4f$ states the relative decrease of c/a in $CeRu_2Si_2$ with respect to the nonhybridized compound is more pronounced than for $CePd_2Si_2$, thus revealing a larger $4f$-hybridization effect on this ratio for the Ru compound than for the other two systems.

As mentioned above, $4f$-$4d$ hybridization together with anisotropy is responsible for the different behaviors shown by the three systems, it is then useful to study in more detail the variation of the Ce-M distances ($d_{\text{Ce-}M}$) with pressure. Figures 2(a) and 2(b) correspond to the calculations without and with $4f$-conduction-band hybridization, respectively. It can be seen that when $4f$ hybridization is turned on, $d_{\text{Ce-}M}$ decreases in the three compounds, as compared to La-M distances ($d_{\text{La-}M}$), indicating that there is a hybridization effect on this variable for the three systems. It can also be observed that the relative effect varies from compound to compound since, at equilibrium, the percent decrease of $d_{\text{Ce-}M}$ with respect to $d_{\text{La-}M}$ is 0.9% in the system with Pd, 1,1% in Rh, and 1.2% in Ru. Under applied pressure this percent variation changes and, for instance, for a 10% volume compression it is of 0.7%, 0.9%, and 1.6%, respectively. From these results, it can be concluded that $d_{\text{Ce-}M}$ decreases faster with pressure with decreasing $4d$ band filling ($\text{Pd}\rightarrow\text{Rh},\rightarrow\text{Ru}$). Taking this into account, we expect the $4f$ hybridization to be more important in $CeRu_2Si_2$ than in $CeRh_2Si_2$ and, in turn, than in $CePd_2Si_2$. This is going to be confirmed in the following sections.

The fact that the c/a ratio of $CeRh_2Si_2$ does not change with applied pressure does not imply that hybridization effects are not present on the other variables such as, for instance, $d_{\text{Ce-}M}$.

B. Spin magnetic moment

We are aware of the underestimation of correlations in our calculations, and that this fact together with the absence of dynamical effects make it impossible to reproduce the ground states of these Ce compounds within this approach. However, the study of the evolution of the spin magnetic

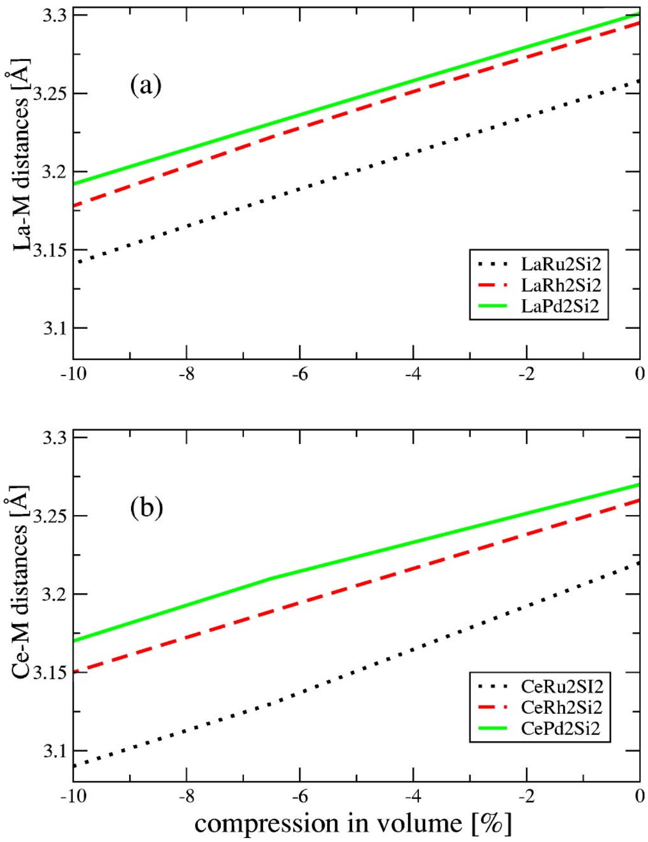

FIG. 2. Evolution of La-M and Ce-M distances with volume compression.

moment of Ce, μ, with pressure within a static band-structure framework, should provide further information on the close relationship between 4*f* conduction-band hybridization (itineracy) and magnetism. For this purpose, only ferromagnetic configurations are being considered and the 4*f* states are being kept in the valence band (hybridized).

In Fig. 3 the calculated spin magnetic moments of Ce for the three systems and their evolution with pressure are depicted. The largest magnetic moment at zero pressure is obtained for the system with Ru. The spin magnetic moment of $CeRh_2Si_2$ follows in magnitude and, finally, the smallest one at equilibrium is the corresponding to the system with Pd.

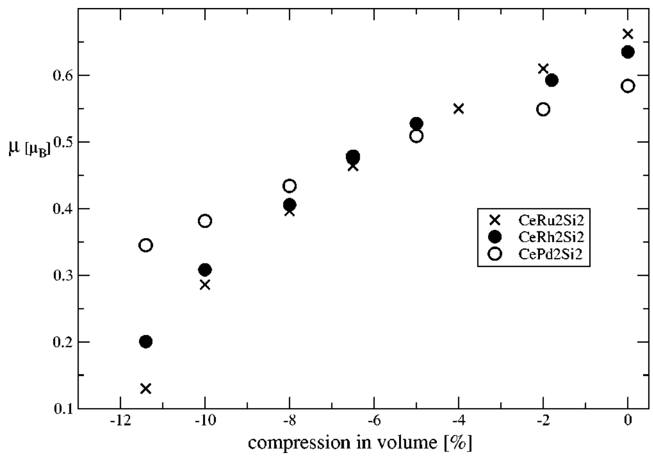

FIG. 3. Evolution of the local spin magnetic moment with pressure.

The magnetic moment of Ce in the system with Ru shows a faster decrease with pressure than the corresponding magnetic moment of the systems with Rh and Pd and this is related to the decrease of the c/a value obtained in the preceding section. The decrease in the c/a ratio leads to reduced Ce-Ru distances. Within the other two compounds the one which loses its Ce magnetic moment next is Rh and finally Pd. This can be associated with an increasing 4*f*-conduction-band hybridization with decreasing 4*d* band filling and explains the observed experimental trends, in particular, the fact that the magnetic order in the system with Rh disappears at lower pressures than in the one with Pd.

V. HYBRIDIZATION FUNCTION

In order to quantify the relative degree of hybridization of the three systems under study, we report in this section the results obtained for the hybridization function $\Gamma(\varepsilon)$, which gives information on the energy distribution of the 4*f*-conduction-band hybridization. Following Refs. 19 and 20, $\Gamma(\varepsilon)$ can be obtained from the *ab initio* calculated projected 4*f* densities of states and it is given by

$$\begin{aligned}\Gamma(\varepsilon) &= -\mathrm{Im}[G_{ff}(\varepsilon - i0)^{-1}]\\ &= -\mathrm{Im}\left[\left\{\int d\varepsilon' \frac{\rho_{ff}(\varepsilon')}{\varepsilon-\varepsilon'-i0}\right\}^{-1}\right].\end{aligned} \tag{1}$$

In Eq. (1), $G_{ff'}$ is the 4*f* Green's function in the *noninteracting* limit and it is estimated using for the spectral density ρ_{ff} the *ab initio* calculated 4*f* densities of states projected onto the Ce site. f and f' label the irreducible representations at this site in the tetragonal point group. In Fig. 4 the total $\Gamma(\varepsilon) = \Sigma\Gamma_{ff}(\varepsilon)$ are plotted for the three compounds. The energy weight of the hybridization function is shifted towards higher energies when M goes from Pd to Ru. This result can be understood if we take into account that the main contributions to the hybridization interaction of the 4*f* states in these compounds is with the 4*d* band of the transition metal *M*. The calculated 4*d* band centers are indicated with arrows, and it can be seen that they are shifted towards higher energies with decreasing 4*d* occupation number. The average 4*f*-hybridization strength is 0.61 eV for Pd, 0.71 eV for Rh, and 0.92 eV for the Ru compound. This monotonous behavior (increasing hybridization strength with decreasing 4*d* band filling and the shift towards the Fermi level) is consistent with what has been reported in the previous sections, that is, with the evolution of μ under pressure and Ce-*M* distances.

The calculated hybridization functions could in principle be used as input for a many-body Hamiltonian in order to obtain the low-energy excitation spectra of the systems considered here.[20]

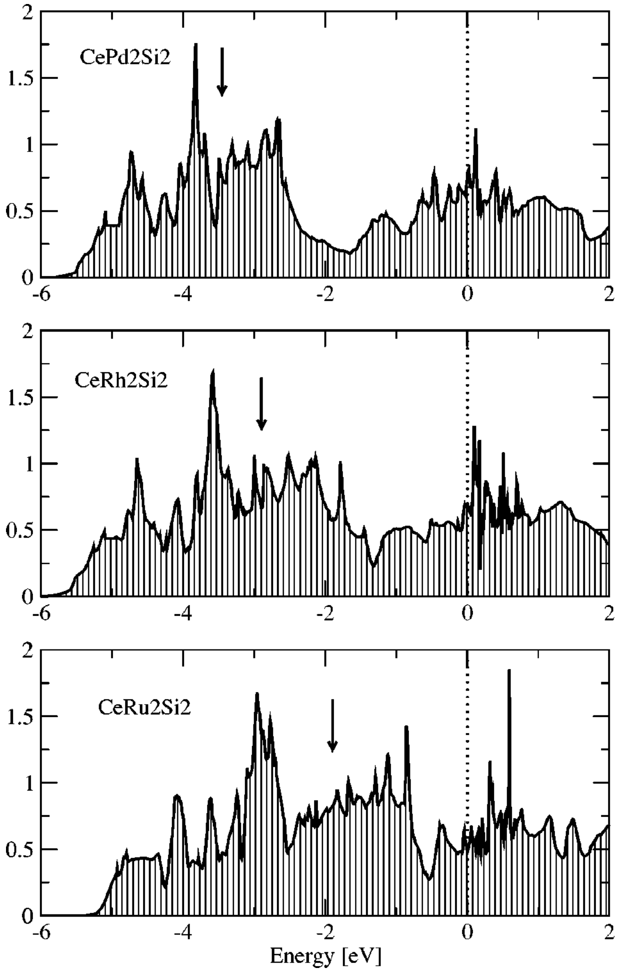

FIG. 4. Total $4f$ hybridization function for CeM_2Si$_2$ with M = Ru, Rh, and Pd. The dot line indicates the Fermi level. The arrow points to the $4d$-band center of the corresponding transition metal M.

VI. DISCUSSION AND CONCLUSIONS

We have calculated structural and electronic properties of CeM_2Si$_2$ systems (M = Ru, Rh, and Pd) within the GGA approximation to density-functional theory. We have compared results coming out from both localized and itinerant treatments of the Ce 's $4f$ electron. They indicate that the structural properties are, in general, in better agreement with experiments for the $4f$ states hybridized with the conduction band (itinerant) than when treated as nonhybridized levels. For instance, this is clearly seen when regarding the evolution of equilibrium volumes along the Ce series as compared to the La one. In all the cases under study, it is clear that the $4f$'s contribute to cohesion.

We stress that from this study we cannot conclude that the $4f$ states are completely itinerant in these compounds, but that they show a degree of hybridization which affects their structural properties in a way which is particular for each system.

We have analyzed the evolution of the c/a ratios with pressure, which remarkably reflects the different characteristic behaviors of each of the three systems. When external pressure is applied the $4f$ states should become increasingly itinerant, and we expect that the experimental evolution of c/a will follow the curves obtained for the respective hybridized calculations. This c/a evolution and the corresponding Ce-M distances, which seem to be related to the competition between the Kondo and the RKKY interactions,[9] have not been measured as a function of pressure. Our results should provide a contribution in the direction of understanding their low-energy many-body physics.

The calculated evolution of Ce-M distances and spin magnetic moment with pressure, together with the obtained hybridization function, indicate that the degree of itineracy in the CeM_2Si$_2$ series increases with decreasing $4d$ band filling.

It is interesting to point out that CeRh$_2$Si$_2$ shows properties which are sensitive to the presence of $4f$ states in the valence band and properties which are not. While it ends up being more hybridized than CePd$_2$Si$_2$, the evolution of its c/a ratio is not affected by $4f$ hybridization, being this an indication of the anisotropy of the interactions present in this compound. These behaviors can be associated with the mentioned controversy between the itinerant and localized nature of the $4f$ state in CeRh$_2$Si$_2$ existing in the literature.[5,6]

Even if only the spin contribution to the magnetic moment is taken into account in the study of the evolution under applied pressure the experimental trends are qualitatively well reproduced (e.g., P_C of the system with Rh is smaller than the one with Pd), and consistent with the studied evolution of the structural properties with pressure and with the relative degree of hybridization of the $4f$ band given by the calculated hybridization functions.

In the studied compounds, many of the unusual and interesting physical properties have their origin in the behavior of the highly correlated $4f$ electrons. In spite of the shortcomings of *ab initio* calculations to describe effects that are dominated by strong correlations, they provide a useful tool to investigate the structural properties of Ce, intermetallic compounds. A detailed information of the electronic structure is necessary to get insight and understanding of their complex behavior and this information should provide reliable inputs for model Hamiltonians which capture the dynamics of the low-energy many-body excitations of these systems.

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