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Volume effects on the magnetic properties of cubic isostructural intermetallics of Ce

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We compare the magnetic behavior of CeAg, CeZn, and CeCd in the ferromagnetic phase under pressure, using total-energy electronic-structure calculations within the local-spin-density approximation. While the calculated magnetic moments at ambient pressure reflect the trend of the unit-cell volumes as the pressure is increased, an instability of the magnetic phase occurs in isovalent CeCd and CeZn at much lower applied pressure than in CeAg, as found by experiments. Results with use of a rigid-band model to fill in the density of states of CeAg with the same number of electrons as CeCd show that the different magnetic behavior of the two compounds is essentially due to a more effective screening of the complete 6*s* shell of Cd. Analogous conclusions are valid for CeZn; the calculated equilibrium volume of the ferromagnetic phase of CeZn is found within the experimental pressure range in which the observed order-order magnetic phase transition takes place.

I. INTRODUCTION

The current interest in most metallic Ce compounds is essentially motivated by the competition between the magnetic Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction[1] and the Kondo[2] effect that characterizes the magnetic properties of these compounds. Because of the complexity of the problem, theoretical approaches rely on models mostly neglecting the actual electronic structure. In these approaches the magnetic and Kondo regimes are characterized by two temperatures,[3] i.e., the Curie (T_C) or Néel (T_N) temperature and the Kondo temperature T_K. The onset of either of the two regimes, or even their coexistence, depends on the relative magnitude of $T_{C,N}$ and T_K. These are determined by the hybridization of the localized Ce 4f states with the extended states[4] as well as by the density of states of the conduction electrons. Therefore, it is possible to drive the crossover from one regime to the other by acting on these two quantities. This has been done experimentally in various Ce systems.[5] It is known[6] that volume reduction generally suppresses magnetism while it increases T_K. The effect of changes in the electron density is, instead, less well understood.[7]

In this paper we will be focusing on CeAg, CeCd, and CeZn, which belong to the class of Ce intermetallics with cubic symmetry. Various experimental investigations were reported on these compounds pointing out anomalies in the magnetic ground state,[8–14] resistivity,[15–17] and transition temperature under pressure,[18–21] which were always interpreted in terms of the RKKY-Kondo competition. These materials exhibit, in addition, a series of interesting magnetic and structural phase transitions as a function of temperature,[10,11,22] applied pressure,[21,23,24] and chemical composition[25] that are not yet very well understood and that need further investigation. Quite surprisingly though, their electronic structure has been ignored until quite recently.[26–28]

All three compounds share the following properties:

(i) They are isostructural in the paramagnetic phase with cubic CsCl structure at normal pressure.

(ii) The paramagnetic-magnetic transition is joined (CeZn) or preceded (CeAg, CeCd) by a modest tetragonal (or orthorhombic) distortion $\simeq 1-2\,\%$.

(iii) The magnetic moment in the ground state is reduced with respect to the expected free-ion or crystal-field value.

(iv) The lattice constants at normal pressure[29] follow the decreasing trend of the metallic ion radii.[30]

Table I summarizes the relevant data collected from various experimental sources and refers to the low-temperature phase at ambient pressure. For CeZn, data under pressure are also reported. The magnetic moments of the three compounds are quite different and, in partic-

TABLE I. Experimental data for CeZn, CeAg, and CeCd. Entries from the second to sixth columns represent the experimental lattice constant, metal atomic radius, magnetic moment per cell, transition temperature, structural transition temperatures ($T_{t,o}$), and ground-state structure.

	a_0 (Å)	R_{met} (Å)	μ/μ_B	$T_{C,N}$ (K)	$T_{t,o}$ (K)	Structure
CeZn	3.70^{a}	1.38^{b}	1.9^{c}	30^{c}	30^{d}	Tet-AFM
			$0.55^{e}, 1.9^{f}$	15^{e}		FM
CeAg	3.75^{a}	1.44^{b}	1.25^{g}	5^{g}	10^{g}	Tet-FM
CeCd	3.86^{a}	1.54^{b}	0.8^{h}	16^{h}	98^{i}	Orth-FM
	3.86^{a}		1.8^{j}			−FM,AFM

[a] Reference 29.
[b] Reference 30.
[c] Reference 8.
[d] Reference 16.
[e] Data referring to $p = 12$ kbar: Ref. 21.
[f] Reference 23.
[g] Reference 10.
[h] Reference 9.
[i] Reference 22.
[j] Reference 12.

ular, they do not scale with the unit-cell volume as one would generally expect.

The situation is particularly puzzling for CeZn that, having the smallest unit volume, shows the largest ground-state magnetic moment[8] and a complicated temperature-pressure phase diagram.[21,23] At ambient pressure, the paramagnetic-antiferromagnetic transition is joined by a tetragonal distortion. If pressure is increased in the ordered phase, T_N decreases until an antiferromagnetic-ferromagnetic phase transition takes place joined by an abrupt drop of T_C and of the sublattice magnetization.[21] A distortion from tetragonal to orthorhombic symmetry with pressure is observed below T_N. The orthorhombic distortion is, however, not bound to the magnetic order-order transition since it is also observed in the paramagnetic phase.[24] We should point out, however, that there is no complete agreement among the experimental results on the value of the magnetic moments[21,23] in the ferromagnetic phase (see Table I).

All these facts stimulate the investigation of the relationship between volume and magnetic properties in these compounds. Moreover, isovalent CeCd and CeZn differ from CeAg by one electron in the external configuration. This situation gives the opportunity to study the interplay between predominantly volume effects, in isovalent CeCd, CeZn, and predominantly electronic effects, in isocore CeCd, CeAg.

This distinction might seem quite artificial since there are volume as well electronic differences between isovalent Cd and Zn and between isocore Ag and Cd. However, one has to bear in mind that isovalent Cd and Zn differ by a filled inner shell, whereas isocore Ag and Cd differ by the filling of the 5*s* shell which directly affects the properties of the Fermi surface. All these different electronic configurations lead, of course, to volume differences as shown in Table I.

We have undertaken all-electron calculations both at ambient and applied pressure. All the results presented in this paper are obtained by the self-consistent full-potential linearized augmented plane-wave (FLAPW) method[31] within the local-spin-density approximation[32] (LSDA). We have also introduced the spin-orbit interaction in the self-consistent[33] cycle for spin-polarized calculations at the experimental equilibrium lattice constants, in order to check how spin-orbit affects the semirelativistic predictions for the magnetic moment.

Since magnetic and structural phase transitions occur in these materials at different pressures and temperatures, we tried to split out the structural from the magnetic contributions to the ground-state properties. This is possible by studying the ground-state properties at fixed structure for the ordered and disordered magnetic phase. The tetragonal and/or orthorhombic distortions to the cubic CsCl structure are quite small. We have therefore chosen the simplest, high-temperature cubic structure. For this fixed symmetry, paramagnetic (PM) and ferromagnetic (FM) calculations are carried out at different hydrostatic pressures. Our aim is to study the relative stability of these phases and to ascertain the main mechanisms that drive the magnetic properties of these compounds.

We are aware that the above assumption may somehow affect the quantitative conclusions on the magnetic behavior. However, we point out that distortions from the cubic symmetry produce very little volume changes and, except for CeZn, occur at a temperature quite higher than the magnetic disorder-order transition. Therefore, direct magnetoelastic effects on the magnetic phase transition may be disregarded in a first approximation. This is also supported by previous linear muffin-tin orbital (LMTO) spin-polarized calculations for CeAg (Ref. 28) which showed negligible differences in the magnetic moment and in the density of states obtained in the cubic and distorted symmetries, as well as by experimental results.[13,15,26]

The assumption of a ferromagnetic ground state for antiferromagnetic CeZn could be strongly questionable. However, as observed experimentally, this is unstable against ferromagnetic order under pressure. This assumption, together with the neglect of the tetragonal distortion, may affect the numerical results for CeZn mainly in the ground state. Nevertheless, we expect the qualitative conclusions to still be valid, as we will show below. The interplay between magnetic order and symmetry lowering in CeZn is certainly a point that should be further investigated but is beyond our present aim.

The paper is organized as follows. In Sec. II, we discuss the electronic structure of the three compounds and give the calculated magnetic moments for the FM structure at the experimental, ambient pressure lattice constant.

In Sec. III, we discuss the effect of pressure on the magnetic behavior. A detailed analysis of CeZn allows us to interpret the order-order transition observed at $p \simeq 12$ kbar.[21,23]

In Sec. IV, we compare our findings with experimental results. In particular, we are able to explain the magnetic behavior induced by isovalent and nonisovalent substitutions in $\mathrm{CeZn}_{1-x}\mathrm{Cd}_x$ and $\mathrm{CeZn}_{1-x}\mathrm{Cu}_x$, respectively.

In Sec. V, we summarize our results and discuss their connection with previous theoretical findings.

II. SPIN-POLARIZED CALCULATIONS AT AMBIENT PRESSURE

The electronic structure of CeZn, CeAg, and CeCd with CsCl structure was obtained[34] assuming the experimental lattice constants: 3.704, 3.755, and 3.855 Å, respectively. The outermost electrons of Ce, including $4f^1$, and those of the metallic ions were treated as valence electrons while the inner shells were treated as core states. The outermost 5*p* states of Ce were treated as valence states since almost 0.1 electrons spilled out of the muffin-tin sphere. The same treatment was used for the semicore 3*d* and 4*d* states of Zn and Cd, respectively. We used a scalar-relativistic scheme in which the core states are self-consistently relaxed and updated at each iteration, by solving the Dirac equation, whereas for the valence states a nonrelativistic equation is solved. Spin-orbit effects on the valence states were included, in the spin-polarized calculation, by means of a self-consistent second variation procedure.[33] We use a plane-wave cutoff of $k_{\max}R_{\mathrm{MT}}=11.02$ a.u. resulting in ~ 320 basis functions at the Brillouin zone center for all compounds. The spin-polarized calculations were performed in the irreducible wedge of the Brillouin zone with a mesh of up to 120 k points within the linear tetrahedron method,[35] with and without spin-orbit interaction in the valence band.

Figure 1 shows the total paramagnetic density of states (DOS) for CeAg [Fig. 1(a)] and CeZn and CeCd [Fig. 1(b)]. As expected from general considerations on the electronic configurations of the component ions and also from previous LMTO calculations on CeAg,[28] the density of states of these compounds is dominated by two contributions. The peak well below the Fermi energy (E_F) originates essentially from the metallic full d shell while the spike around E_F is due to the Ce 4f states. Other contributions, much smaller on this scale, come from the d,s states of Ce and the p,s states of the metal. Notice the deeper position of the cation semicore d shell in CeCd with respect to CeAg due to screening effect of the outermost filled s shell of Cd.

In the ferromagnetic phase, the states significantly affected by the exchange interaction are the Ce f's and d's. Plots of their majority and minority partial $(l=2,3)$ spin density of states (PDOS) are shown in Fig. 2 for CeAg and in Fig. 3 for CeZn and CeCd. It is interesting to see that the shape of the f peak with the characteristic satellite peak just below E_F in the majority spin component is a common feature in all three compounds. Isovalent CeZn and CeCd show very similar d spin density of states: the CeZn d states, below the Fermi level, look rigidly shifted toward lower energies compared to analogous structures in CeCd. This is ascribable to a stronger bonding effect of Ce d states hybridized with the more shallow semicore d shell of Zn, compared with Cd. At the Fermi level, there are significant differences in the DOS.

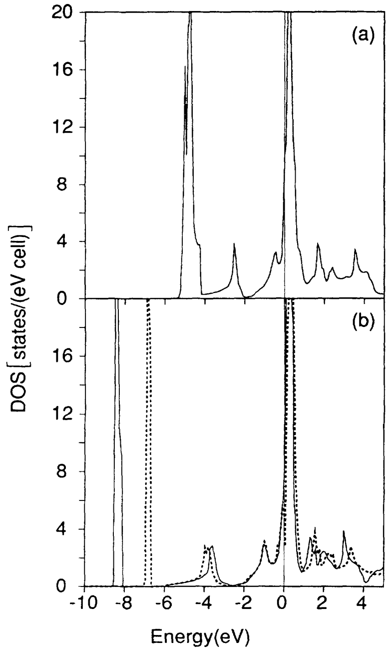

FIG. 1. Paramagnetic total density of states for (a) CeAg and (b) CeCd (solid line), CeZn (dashed line) at normal pressure. The crystal symmetry is cubic CsCl and the lattice constants are those in Table I.

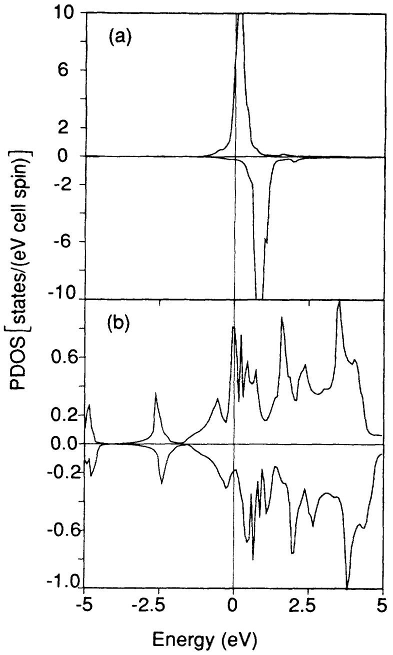

FIG. 2. Majority and minority Ce (a) f and (b) d partial spin density of states at normal pressure in CeAg. The Fermi energy is taken as the zero of the energy scale.

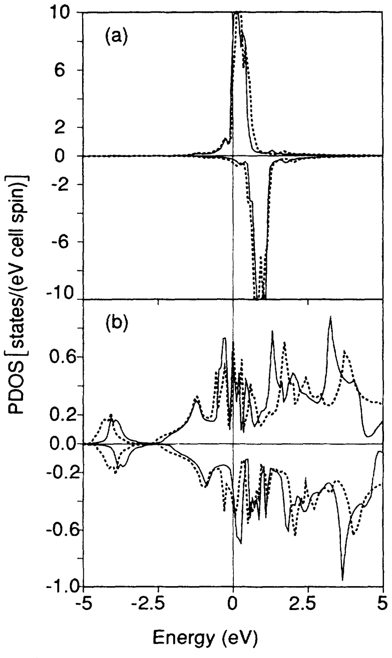

FIG. 3. Majority and minority (a) Ce f and (b) d partial spin density of states at normal pressure in CeCd (solid line), CeZn (dashed line). The Fermi energy is taken as the zero of the energy scale.

TABLE II. Charge decomposition (in electrons/unit cell) into different l angular momentum components inside the muffin-tin spheres for all three compounds considered in the ferromagnetic phase and at the experimental lattice constant.

		l component			
Compound	Atom	Q_s	Q_p	Q_d	Q_f
CeZn	Ce	0.25	5.94	1.12	1.13
	Zn	1.10	0.74	9.92	0.02
CeAg	Ce	0.26	5.94	1.07	1.19
	Ag	0.83	0.46	9.38	0.02
CeCd	Ce	0.24	5.93	1.12	1.16
	Cd	0.97	0.63	9.77	0.01

In Table II, we report the l decomposed charge for each atom in the three cases. The Ce f charge Q_f is practically the same in all cases, whereas the Ce d charge Q_d on Ce increases in CeCd and CeZn by about 10 and 20 %, respectively, compared to CeAg. It should also be noticed that the second s electron in the valence band of CeZn and CeCd, absent in Ag results as increased Q_s, Q_p, and, to a lesser extent, Q_d charge on the metal atom.

In Table III, we list the magnetic moments, at different lattice constants, calculated integrating the majority- and minority-spin components up to E_F. Inclusion of relativistic effects did not affect the total magnetic moment significantly: we find increased Ce f and d contributions to the total moment by about $0.03\mu_B$, which is close to our numerical error. Error bars on the calculated magnetic moments due to the cutoff in the parameters considered in the convergence are about $0.02\mu_B$.

The entries relative to the experimental lattice constant a_0, italic in Table III, indicate that the f and d states of Ce provide the main contribution to the magnetic moment in all three cases.

The total moment μ_T, essentially due to the Ce f component, reflects the unit-cell volume trend as expected theoretically: it increases in going from CeZn to CeCd. Let us take the volume as a quantitative criterion of interpretation of Table III. Under this assumption we would expect the ratio of the total moments for any pair of compounds to follow linearly the ratio of the corresponding volumes. This is not the case for the entries of Table III since CeAg shows a large moment per unit volume. In particular, CeAg has the largest f contribution to μ_T, at least for the ambient pressure volume. This indicates that electronic effects may play a significant role on the magnetic properties, more than volume effects alone.

TABLE III. Total magnetic moment per f.u., Ce f,d and total components (in Bohr magnetons μ_B), and Stoner factor (S) vs lattice constant. Italic entries refer to the experimental lattice constants (a_0).

	a (Å)	μ_T/μ_B	μ_f^{Ce}/μ_B	μ_d^{Ce}/μ_B	μ_T^{Ce}/μ_B	S
CeZn	3.361	0.45	0.36	0.04	0.41	0.30
	3.510	0.82	0.61	0.10	0.71	0.48
	3.544	0.90	0.66	0.11	0.78	0.57
	3.704	0.89	0.68	0.09	0.77	0.89
	3.855	1.04	0.81	0.09	0.90	1.23
CeAg	3.387	0.84	0.57	0.14	0.71	0.83
	3.544	0.89	0.64	0.13	0.78	1.05
	3.567	0.96	0.70	0.14	0.84	1.11
	3.755	1.13	0.87	0.12	0.99	1.50
CeCd	3.387	0.56	0.41	0.08	0.49	0.37
	3.553	1.01	0.64	0.19	0.84	0.51
	3.704	1.31	0.81	0.24	1.06	0.78
	3.855	1.35	0.87	0.21	1.09	1.36

Finally, the small μ_f,μ_T found in CeZn is due to a small-f spin polarization rather than to a lower Q_f (see Table II). This is also suggested by the PDOS in Figs. 2 and 3.

III. SPIN-POLARIZED CALCULATION AT APPLIED PRESSURE

Magnetic measurements on CeCd, CeAg, and CeZn under pressure have revealed a tendency to instability of the ground-state magnetic phase. This instability is shown by a decrease of the transition temperature with respect to the ambient pressure value.

In CeCd, T_C decreases monotonically with increasing pressure with a tendency to saturate at higher pressure ($\simeq 12$ kbar).[17] In CeAg, the $T_C(p)$ curve is not linear:[20,19] it first increases, between 0 and 5 kbar, then drops to zero between 30 and 40 kbar. In CeZn, pressure induces a transition from the AF state to a FM state (at $\simeq 12$ kbar) with a large drop of the transition temperature and also of the magnetic moment as found by Kadomatsu *et al.*[21] but not confirmed by Shigeoka *et al.*[23] This transition is joined by a structural change also occurring above T_C and therefore is independent of the magnetic transition.[24]

All these features have been ascribed to the enhancement of the s-f coupling constant between f and band states occurring in the RKKY and Kondo models. The smoother or steeper decrease in T_C would be a balancing effect of other parameters in the RKKY interaction due to peculiarities in the density of states.

We have attacked the problem of the magnetic phase stability on the ground of purely electronic structure considerations. We have performed calculations at the reduced lattice constants, listed in Table III, to reproduce the effect of an applied hydrostatic pressure. We quote that at the maximum reduction ($\simeq 10\%$) of the experimental volume corresponds a calculated pressure between 200 and 300 kbar, obtained using the calculated bulk modulus for each compound. Self-consistent calculations for the PM and FM phases at each lattice constant were done in the same numerical conditions described in the previous section. For each volume, the magnetic moment, the Stoner factor, reported in Table III, and the total energy were calculated. The behavior of the magnetic moment versus volume reduction is shown in Fig. 4. Here we plotted, for the three compounds, the quantity $\mu_T(a)/\mu_T(a_0)$ as a function of the ratio a/a_0, where a and a_0 are the lattice constants at applied and normal

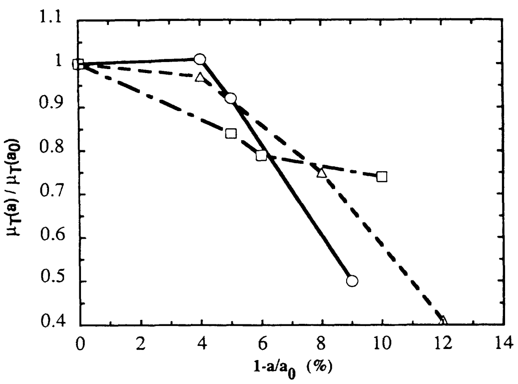

FIG. 4. Plot of the quantity $\mu_T(a)/\mu_T(a_0)$ as a function of a/a_0 for CeZn (circles), CeAg (squares), and CeCd (triangles). The lines connecting the calculated values are drown as a guide to the eyes only. Notice the drop of $\mu_T^{Ce}(a)/\mu_T(a_0)$ at the critical value of the abscissa $a/a_0 \simeq 95\%$.

pressures, respectively, and $\mu_T(a)$ represents the total magnetic moment at a given lattice constant a.

The quantity plotted in Fig. 4 gives a comparative trend of the volume dependence of the magnetic moment in the three compounds. We see that, in all cases there is a change in the slope for more than 5% volume decrease, with CeZn and CeCd having similar behavior and a steeper drop. The calculated pressure values corresponding to this volume range between 10 and 20 kbar depending on the compound and is within the pressures obtained experimentally.

The plot of Fig. 4 shows a larger instability of the magnetic moment at high pressure for CeCd and CeZn compared to CeAg. In particular, the moment in CeZn extrapolates to zero at higher pressures. This is consistent with the Stoner factor in the PM phase and with the results of total-energy calculations. In fact, we find that, while in CeAg, the FM phase has always lower total energy than the PM phase at any pressure, in CeCd and CeZn it becomes unstable for a volume reduction larger than about 3%.

We would like to mention that our theoretical findings for CeZn seem to support the experimental results by Kadomatsu *et al.*,[21] showing a strong reduction of the magnetic moment at the transition pressure [$\mu = 0.55\mu_B$/Ce atom (Ref. 21)]. We do find, indeed, that the system might be driven toward a paramagnetic phase, the Stoner factor being quite small. At present, we do not find any evidence that might support the onset of a well-established, stable, FM phase with such a high magnetic moment as found by more recent measurements [$\mu = 1.6\mu_B$/Ce atom (Ref. 23)]. However, having in mind the assumptions made on the structure and the magnetic phase as well as the limitations of LSDA, we cannot completely rule out the presence of this high moment FM phase. Still, the discrepancy between the two different experimental findings deserves, in our opinion, more careful considerations; the role played by external magnetic fields (and consequent magnetic hysteresis) and the possible coexistence of different magnetic phases with different magnetic moments (as also mentioned in Ref. 23) should be thoroughly investigated.

We have looked for possible f charge delocalization with increasing pressure as a possible cause of the f moment reduction. At the smallest volume considered, we find $Q_f = 1.10$, 1.16, and 1.12 electrons per Ce atom in CeZn, CeAg, and CeCd, respectively. Comparing with the ambient pressure values in Table II, we conclude that no significant f charge delocalization has been induced by volume reduction in any compound. This is in agreement with the results of the partial Ce moment in Table III and indicates that the f electron stays rather localized, even under pressure.

The large moment drop with pressure occurring in CeZn and CeCd deserves a more detailed analysis. In these isovalent compounds there seems to be a threshold value of the lattice constant, estimated as $a \simeq 96\%$ a_0 from Fig. 4. Above this value, the moment follows the volume trend as at normal pressure. For further volume reduction, the magnetic moment decreases quicker in CeCd and in CeZn than in CeAg. At this threshold there is also a drop in the Ce d contribution to μ_T in CeCd and CeZn, which is not found in CeAg. For $a \simeq 3.5$ Å (see Table III), the different l contributions to the total magnetic moment are still comparable in the three compounds. Since, as stated above, no significant charge delocalization occurs under pressure, the mechanism of moment reduction has to be ascribed merely to a weaker exchange interaction between f up- and down-spin components, which is more evident in CeZn and CeCd.

These observations suggest that, beyond a critical volume, electronic effects dominate over pure volume effects. The only difference between CeAg and isovalent CeCd and CeZn is the full outer s shell of the metal in the latter ones. This enhances the screening, as observed before, and weakens the exchange field between f up and down components. Moreover, a direct effect on the magnetism may also be due to the larger absolute number of conduction electrons in CeCd and CeZn which affects the Fermi surface and the value of the DOS at E_F.

To ascertain this point more quantitatively, we have tried to compare CeAg and CeCd on a pure electronic basis. Since these compounds have an identical number of core electrons, it is possible to monitor just the effect of the second 6s electron of Cd with respect to Ag by analyzing the DOS of CeAg and CeCd at the same volume. Choosing $a = 3.54$ Å, we have filled the DOS of CeAg with one more electron, following a rigid-band approach. The situation is illustrated in Fig. 5 where the DOS of CeAg and CeCd are reported in the upper and lower panel, respectively. The Fermi level, taken as the zero of the energy scale, is now obtained with the same number of electrons in both cases. By filling the DOS of CeAg with the extra electron, E_F is pushed toward the huge second f peak in the majority DOS. This leads to a very high contribution from the majority component which is not balanced by the minority DOS. As a result, the magnetic moment grows up to $1.53\mu_B$. This value exceeds by far the value of μ_T in CeCd, which amounts to $\simeq 1\mu_B$ only, at this volume. This dramatic increase is essentially due to the following Ce charge components:

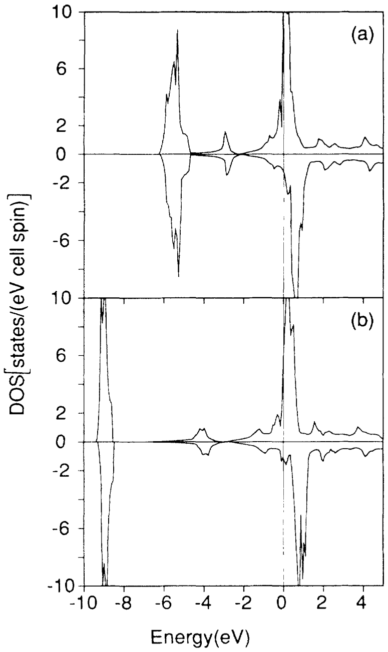

FIG. 5. Comparison of the majority and minority DOS for (a) CeAg and (b) CeCd at the same volume corresponding to the third a/a_0 value in Fig. 4. The Fermi level in CeAg is obtained by filling rigidly the corresponding DOS with the same number of electrons as in CeCd. The Fermi level in real CeAg occurs, in this scale, just at the minimum of the majority component below the energy zero.

majority and minority f amounting to 1.55 and 0.32, respectively; majority and minority d amounting to 0.71 and 0.56, respectively.

Another interesting quantity to look at is the value of the total density of states at E_F that we indicate by $\rho_{\downarrow(\uparrow)}$. We find $\rho_\uparrow = 132.1$ and $\rho_\downarrow = 20.5$ for CeAg plus one electron, against $\rho_\uparrow = 82.6$ and $\rho_\downarrow = 21.1$ in CeCd.

The fact that a simple rigid-band picture cannot reproduce the electronic and magnetic properties of CeCd starting from those of CeAg indicates that the screening effects due to the extra electron are very important in determining the different magnetic behaviors of CeAg and CeCd. The second 6s electron is not only responsible for a different band filling, but it also modifies substantially the band structure of the compound. A comparison with CeZn gives analogous results, despite the different electronic core.

The last point we have investigated is the order-order magnetic phase transition observed in CeZn. In the present approach we neglect AF order. We expect, nevertheless, to find insights on this transition by looking at the total energy for the PM and FM phases as the volume is changed. The resulting curves are reported in Fig. 6. We observe that the calculated equilibrium lattice constant for the FM and PM phases is $a_0^{\text{theor}} = 3.54$ Å (the two total-energy curves are very close in energy and barely distinguishable within our numerical accuracy). Using a Murnaghan[36] fit of our total-energy curve, we obtain, for the bulk modulus and its pressure derivative, $B_0^{\text{theor}} = 651.1$ kbar and $B_0' = 4.8$, respectively. From the value of the compressibility measured very recently,[24] $K = 1.71 \times 10^{-2}$ GPa^{-1}, we deduce $B_0 = 1/K = 585$ kbar, which is in good agreement with B_0^{theor} quoted above. Using this theoretical value, we are able to find that the pressure corresponding to our a_0^{theor} for the PM and FM phases is about 12 kbar. This coincides with the pressure at which the transition from AF to FM (through a PM phase) occurs[37] ($p \sim 8-12$ kbar).[21,23] Notice that the experimental pressure value is well recovered theoretically even neglecting distortion effects. We expect that a full account of the complete phase diagram observed for CeZn (Ref. 23) can be obtained theoretically by extending our present calculations to the AF phase in the actual distorted symmetry.

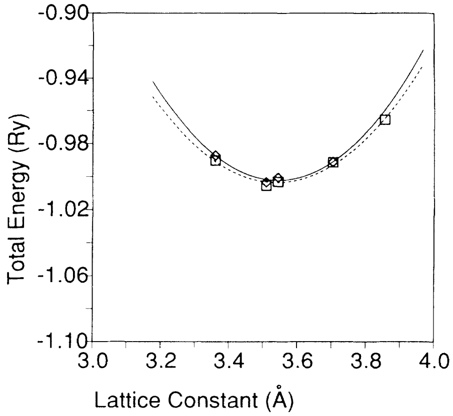

FIG. 6. Total energy vs lattice constant calculation for the paramagnetic (triangles) and FM (squares) phases in CeZn.

IV. COMPARISON WITH EXPERIMENTS

When comparing our results with experiments, we find a satisfactory agreement for the general trend of the magnetic properties observed in these compounds as well as some quantitative agreement in particular cases. In addition, as shown below, our present study allows one to understand the magnetic behavior of two substitutional ternary alloys.

The three compounds were found to be magnetically unstable under pressure, as shown by the behavior of the magnetic temperatures ($T_{C,N}$) as a function of pressure. For CeCd and CeZn, the instability sets in at a much lower pressure than in CeAg, in qualitative agreement with our present findings.

In CeZn, moreover, a magnetic order-order transition has been observed experimentally for an applied pressure of about 12 kbar.[21,23] By total-energy calculations we have obtained a bulk modulus corresponding to a compressibility value in good agreement with very recent measurements.[24] We have also found that the pressure value corresponding to our theoretical FM (and PM) equilibrium constant corresponds to the experimental value for the magnetic transition found in Refs. 21 and

23. The experimental magnetic moments at ambient pressure of AFM CeZn and FM CeCd (see Table I) do not agree with our theoretical values (see Table III).

As far as CeZn is concerned, we should mention that a direct comparison with experiments regarding the magnetic moment at the experimental volume is not possible since the observed phase is AFM rather than FM, as we assumed. Moreover, as mentioned earlier, the tetragonal distortion might be crucial in recovering the correct sublattice magnetic moment value in the AFM phase. However, we recall that our calculations correctly recover the magnetic behavior of CeZn under pressure as reported by experiments[21,23] (see discussion in Sec. III).

In the CeCd case, we point out that there is no unique agreement on the ground-state configuration, since both FM (Ref. 9) and AFM (Ref. 12) states have been reported and that the experimental measurements on this specific compound are usually complicated by its difficult metallurgic synthesis.[41]

For CeAg we find a good agreement, within a few percent, with the experimental magnetic moment.[10] This improves substantially the previous LMTO result.[28]

Using our study on volume and electronic effects on the magnetic properties, we may gain some insight on the behavior of the two substituted systems, $\text{CeZn}_{1-x}\text{Cd}_x$ (Ref. 25) and $\text{CeZn}_{1-x}\text{Cu}_x$.[38] In the former system, substitution of Zn by isovalent Cd acts essentially as CeZn volume enhancement for $0 \leq x \leq 0.5$. In this range, the AFM structure holds, as in pure CeZn, T_N decreases very slightly but the magnetization increases (see Fig. 1 of Ref. 24). From our calculation for CeZn at an expanded lattice constant equal to the CeCd experimental one, we find about an 11% increase of the CeZn magnetic moment (see Table III). Notice that the lattice constant of $\text{CeZn}_{0.5}\text{Cd}_{0.5}$ may be estimated to be about 3.78 Å.

For $0.6 \leq x \leq 1$, the system under T_C is FM, as pure CeCd, the spontaneous magnetization is $0.8\mu_B$ and is almost independent of x (see Fig. 1 of Ref. 25). In this concentration range the system may be seen as compressed CeCd. Estimating the lattice constant for the system at $x = 0.6$ by an average of the experimental values for CeCd and CeZn quoted in Table I, we find $a = 3.8$ Å. This corresponds to $a/a_0 = 0.98$ in Fig. 4, where practically no decrease in the CeCd magnetic moment occurs.

The magnetic behavior of $\text{CeZn}_{1-x}\text{Cu}_x$ was experimentally investigated[38] in the range $0 \leq x \leq 0.6$ and can be summarized as follows. For $x \leq 0.2$, the AFM phase is stable as in pure CeZn with a slightly decreased magnetic moment.

As x increases between 0.2 and 0.6, the magnetic moment undergoes a continuous drop while a ferromagnetic component grows, resulting in an overall ferrimagnetic phase (see Fig. 3 of Ref. 37). This behavior has been ascribed by Uwakoto *et al.*[38] to the enhancement of the s-f hybridization due to substitution of Zn by Cu. In fact, CeCu_2 is known to be an ordered Kondo lattice with a magnetic transition temperature[39] of only 3.5 K. However, since CeCu_2 orders antiferromagnetically as well as CeZn, the observation of ferromagnetism by Uwakoto *et al.*[38] in $\text{CeZn}_{0.4}\text{Cu}_{0.6}$ raises some questions. We may tentatively interpret the behavior of $\text{CeZn}_{1-x}\text{Cu}_x$ in terms of a combination of volume and electronic density-of-states effects. In fact the Cu ion is smaller than Zn, having the same core but is isovalent to Ag. Therefore, we might expect that, for $x \leq 0.2$, volume effects are predominant and the magnetic moment behaves as in compressed CeZn. We suggest that the more complex behavior beyond $x = 0.2$ might be interpreted in terms of changes in the density of states as shown by the rigid-band model comparison of CeAg and CeCd. This interpretation, as well as the one for the Ce-Zn-Cd system, does not exclude the presence of a Kondo effect.

V. CONCLUSIONS

We have performed extended electronic-structure calculations on isostructural CeZn, CeAg, and CeCd under pressure to ascertain the role played by volume effects on the magnetic properties of these compounds. In particular, we have tried to analyze the causes that drive the magnetic instability observed in these compounds. The instability was interpreted qualitatively, so far, in terms of the competition between the RKKY interaction and the Kondo compensation of the magnetic moment, being well known that the Kondo effect is enhanced by volume reduction.

Although, by its very nature, one-electron LSDA calculations alone cannot be conclusive about the presence of a Kondo effect, they should be taken into account as the basic framework for any further interpretation of real compounds. In particular, we find presently that the f states are localized at any pressure and that variations of the electronic density as well as of the volume affect the stability of the magnetic phase. This supports the hypothesis of the RKKY-Kondo competition. Notice that, in GdAg, a prototype of the normal RKKY magnetic behavior, pressure does not induce any magnetic instability.[20] Our analysis was carried out as follows.

Using spin-polarized calculations, we obtain the magnetic moment as a function of volume reduction starting from the experimental lattice constant. We found that the magnetic moments of the three compounds at ambient pressure reflect the trend of the unit-cell volumes, i.e., increase in going from CeZn to CeCd. The magnetic moment per unit volume, however, is largest for CeAg.

The quantitative analysis of the different atomic and l-decomposed contributions to the total moment show that the Ce f's accounts for at least 90% of the total moment, in all cases. This result agrees with the idea of localized f electrons as found by previous LMTO calculations for CeAg (Ref. 28) and by very recent photoemission results.[27]

When pressure is applied, up to the maximum volume reduction by 10%, the magnetic moment decreases in all cases, with a change of slope at about 96% a_0 (see Fig. 4). The moment drop is essentially due to a drop in the absolute f contribution caused by lowering of the exchange interaction and not by delocalization of the f states. This is shown by the l-decomposed charge on each atom that stays constant under compression, in agreement with analogous results found for CeAg under pressure.[40]

As shown in Fig. 4, isovalent CeZn and CeCd display a comparable behavior under pressure, i.e., a much steeper moment decrease as well as a much more pronounced Stoner instability than CeAg. Moreover, the relative contribution μ_f to the total moment is different from that of CeAg. Since the three compounds are practically isovolumic where the abrupt slope change occurs, we argued that the origin should be searched in the different filling of the outermost s shell in Ag (s^1) and in Cd,Zn (s^2).

To ascertain this point, we have compared the DOS of CeAg and CeCd at the same volume and with the same number of electrons finding that the density of states at the Fermi level and the magnetic moment of real CeCd are much lower. This shows that it is generally incorrect to extrapolate conclusions on the electronic properties of different compounds from their similar magnetic behavior, as done in Ref. 17 for CeCd. We have also calculated the magnetic moment that would correspond to CeCd obtain by adding one electron to the DOS of CeAg. This gives a moment 50% larger than the calculated for the real CeCd. We therefore conclude that the larger screening by the Cd $6s^2$ shell in CeCd weakens the exchange interaction among f up and down components and enhances the magnetic instability. It would be very interesting to study the behavior of substituted Ce-Ag-Cd systems experimentally. Analogous conclusions hold for CeZn.

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