RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 21 1 JUNE 1993-I

Magnetic instabilities in Ce compounds: Effect of pressure and chemical substitutions

Patrizia Monachesi and Alessandra Continenza
Dipartimento di Fisica, Universitá dell'Aquila, I-67100 L'Aquila, Italy

(Received 8 March 1993)

Many intermetallic Ce compounds have magnetic ground states unstable under pressure and vs anion concentration in alloys. We analyze the magnetic instability by calculating the magnetic moment in the local spin density approximation and the *hybridization* width Δ of the Anderson model as a function of volume reduction and composition in $\mathrm{CeCd}_{1-x}\mathrm{Zn}_x$, $\mathrm{CeAg}_{1-x}\mathrm{Zn}_x$, and $\mathrm{CeCd}_{1-x}\mathrm{Ag}_x$. For x=0, Δ is found to increase with volume reduction, as expected. Our calculations may thus explain the behavior of T_C vs pressure observed in CeAg in terms of the RKKY-Kondo competition driven by the increase of the s-f coupling. In the case of ternary solid solutions, the behavior of Δ vs volume contraction is opposite to that expected from electronic pressure considerations in $\mathrm{CeAg}_{1-x}\mathrm{Zn}_x$ and $\mathrm{CeCd}_{1-x}\mathrm{Zn}_x$, pointing to the predominance of electronic effects in alloys. This may explain the behavior of the magnetic moment and transition temperature observed in the latter compound and qualitatively in $\mathrm{Ce(Rh}_{1-x}\mathrm{Ru}_x)\mathrm{Si}_2$ and $\mathrm{U(Rh}_{1-x}\mathrm{Ru}_x)\mathrm{Si}_2$. We carry out calculations of Δ and of the magnetic moment vs pressure also for GdAg, which is a ferromagnet with stable f moments. The comparison with its Ce counterpart underlines the different behavior of the f electrons to determine the magnetic stability of the two compounds.

More and more Ce and U compounds, considered as moderate or strong heavy fermion systems, are found to have a magnetic ground state unstable against pressure or alloying.[1] The instability manifests itself as a variation of the Curie (Néel) temperature and of the low-temperature magnetic moment.

The origin of this magnetic instability may be drawn back to the competition between two effects:[2] the magnetic RKKY interaction, tending to order the localized f moments, and the Kondo screening, tending to wash them out. Both effects originate from the antiferromagnetic[3,4] s-f exchange coupling $J_{s\text{-}f}$ (Ref. 5) which depends on the *hybridization*[6] among conduction and localized f states and from the position of the f state relative to the Fermi energy. $J_{s\text{-}f}$ depends on volume, essentially through the hybridization and the density of states $\rho(E)$: it is known to increase with volume reduction.[7] The instability can be therefore driven by presssure.[8]

In substitutional systems, however, chemical substitutions also affect $J_{s\text{-}f}$ through electronic pressure and changes in the density of states. These latter ones may overwhelm the effect of volume variations due to electronic pressure, particularly in systems where substitutions are not isovalent. An example is given by the two isostructural compounds $\mathrm{Ce(Rh}_{1-x}\mathrm{Ru}_x)\mathrm{Si}_2$ (Ref. 9) and $\mathrm{U(Rh}_{1-x}\mathrm{Ru}_x)\mathrm{Si}_2$,[10] where a decrease of the magnetic moment and transition temperature is recorded despite an increase of volume with x.

In this paper we investigate theoretically the relationship between *hybridization*-volume-electronic structure and the magnetic instability observed in Ce compounds with Ag, Cd, Zn.

Among these compounds, claimed to behave as Kondo lattices, CeAg shows the characteristic behavior of T_C vs pressure[11] ascribable to the forementioned RKKY-Kondo competition in the region of the crossover. Also for CeZn (Ref. 12) and CeCd (Ref. 13) pressure induces a decrease in the magnetic transition temperature but with a less clear fingerprint of a Kondo effect.

In isostructural stable f-moment systems, like GdAg (Ref. 11) where the RKKY interaction is due to a positive s-f coupling, pressure has practically no effect on the magnetic stability.[8] We therefore carry out calculations also for GdAg to have a reference ferromagnet where the Kondo effect can be safely ruled out.

We have attacked the problem using different approaches: (i) we perform electronic structure calculations in local spin density approximation (LSDA) and calculate the magnetic moment of each compound as a function of volume; (ii) we apply the Anderson model to calculate the hybridization width Δ. In particular, we compare the effect of pressure (i.e., volume reduction) and chemical substitution (i.e., alloying) on Δ for such real systems.

Following the first approach,[14] we find some quantitative agreement with the experiments for CeZn and CeAg. However, as far as the magnetic instabilty is concerned, the persistence of a non-negligible magnetic moment calculated for a very compressed volume in CeAg does not agree with the vanishing of the magnetic order observed experimentally.[11]

With the second approach we find that the behavior of CeAg can be understood[15] in terms of the large increase of the *hybridization* width $\Delta(E_F)$ as a function of lattice reduction. For all the three Ce compounds we find a stronger dependence of Δ on composition than on volume. Our results show quite clearly that the *hybridization*, and hence the $J_{s\text{-}f}$ coupling, does not scale in any simple way with the volume in these isostructural compounds.

Finally, the results for GdAg agree with the experiments and with the picture of a stable f system, confirming that our theoretical calculations are capable to account for the different nature of the magnetic interactions in both Kondo systems and stable moment systems.

RESULTS

Paramagnetic and spin-polarized electronic structure calculations, both at equilibrium and reduced volume, have been carried out using the full potential linearized augmented plane wave (FLAPW) method within LSDA.[16]

In Fig. 1 we show the plot of the normalized magnetic moment for cubic CeAg, CeCd, and CeZn vs lattice constant variation, obtained directly from spin-polarized calculations. According to this plot, CeCd and CeZn behave similarly in agreement with the fact that they are isovalent and therefore have very close density of states (see Figs. 1 and 2 of Ref. 14). In particular, both compounds undergo a substantial moment reduction at the smallest volume. This behavior is somewhat in agreement with the experiments for CeZn,[14] that undergoes an antiferromagnetic-ferromagnetic phase transition with a drop (see Fig. 7 of Ref. 12) of the magnetic moment. For CeCd no data on the magnetic moment vs pressure are available, but the T_C vs pressure curve shows a monotonic, smooth decrease[13] indicating a weakening of the magnetic coupling.

For CeAg, whose calculated[14] and measured[17] equilibrium magnetic moment agree within 10%, a discrepancy is found among theoretical and experimental behavior under pressure. In fact, as shown in Fig. 1, CeAg keeps a non-negligible magnetization even at the highest volume reduction. Since in the present LSDA calculations, the magnetic moment decrease is ascribable to a decrease of the exchange integral between essentially the Ce f moments, the result of Fig. 1 for CeAg is in contrast with the vanishing of T_C at high pressure observed by Eiling and Schilling.[11]

In Fig. 1 we report also the magnetic moment of GdAg at equilibrium and reduced volume, obtained from spin-polarized calculations. No appreciable change is found, in this case, in agreement with experiments[11] and with the different origin of the RKKY interaction[5,8] in this material.

To take account of the Kondo-lattice effect we have assumed the dimensionless coupling parameter $\rho(E_F)J_{s\text{-}f} \simeq -\frac{\Delta(E_F)}{(E_F-E_f)}$ to depend on volume essentially through the hybridization width at the Fermi energy $\Delta(E_F)$, neglecting the small (positive) dependence[15,18] of E_F-E_f on volume (here, E_F and E_f are the Fermi and f-state energy, respectively). Also in the case of ternary alloys E_F-E_f may be assumed not to change much with anion substitution.

We define the energy-dependent *hybridization* width $\Delta(E)$ as

$$\Delta(E) = \frac{1}{N_\Gamma}\pi \, \mathrm{tr}_m \Sigma_{n\mathbf{k}\sigma} |V_{m,n\mathbf{k}\sigma}|^2 \delta(E - E_{n\mathbf{k}\sigma}), \qquad (1)$$

where N_Γ and Γ denote the multiplicity and the representation of the manyfold f state of the Ce f^1 ground state, respectively.

As described elsewhere,[19] the matrix elements $V_{m,n\mathbf{k}\sigma}$ in Eq. (1) are calculated by implementation of *ab initio* electronic structure calculations within LSDA. Through a linear combination of atomic orbitals (LCAO) fit to the self-consistent paramagnetic band structure, we calculate the single $V_{m,n\mathbf{k}\sigma}$ matrix elements from the Slater-Koster parameters for each binary compound at different unit cell volume. The approximations involved in this procedure and the accuracy of the fit have been discussed previously.[19]

In Fig. 2 we report the normalized hybridization width at the Fermi level $\Delta_F(a)/\Delta_F(a_0)$ as a function of lattice constant reduction. According to our simplified assumption above, the plotted quantity describes the variation of the dimensionless s-f coupling with pressure. As expected for Kondo systems, Δ_F increases with volume reduction for the three Ce compounds. Notice, however, that since actual lattice constant variations attainable with medium-high pressure fall below the abscissa value of 6%, Fig. 2 suggests that Kondo-RKKY competition is

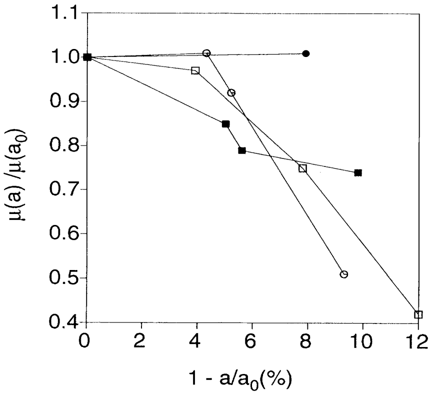

FIG. 1. Magnetic moment $\mu(a)/\mu(a_0)$, normalized to its equilibrium value at a_0, as a function of lattice constant reduction (percent) for CeCd (empty squares), CeZn (empty circles), CeAg (full squares), and GdAg (full circles). The lines are guidelines for the eye.

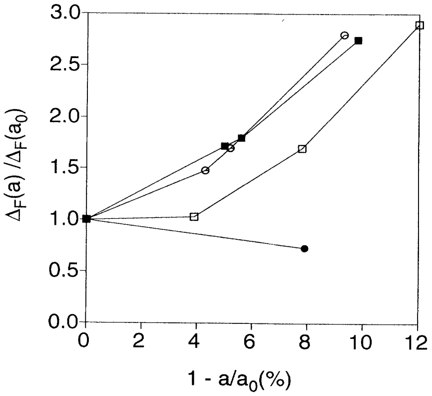

FIG. 2. Hybridization width, normalized to its equilibrium value at a_0, at the Fermi energy $\Delta_F(a)/\Delta_F(a_0)$, as a function of lattice constant reduction (percent) for CeCd, CeZn, CeAg, and GdAg. Symbols are as above. The lines are guidelines for the eye.

smoother in CeCd. CeZn and CeAg, despite the different external electronic configurations, behave in a similar way in this case and show a steep increase of $\Delta_F(a)$ with volume reduction. Figure 2 supports the idea that the behavior of T_C with pressure found by Eiling and Schilling[11] in CeAg is due to the crossover from RKKY to the Kondo lattice regime. In fact, for increasing Δ_F, both T_K and T_C increase until T_K, for a critical value of Δ, takes over.[2] Thereafter, the f moments start to be screened out with consequent weakening of the magnetic interaction.

We have calculated the hybridization width also for GdAg, expecting completely different results from its Ce counterpart. This is indeed the case as displayed in Fig. 2: $\Delta_F(a)/\Delta_F(a_0)$ for GdAg has a negative slope. For the sake of further comparison we report plots of $\Delta(E)$ for GdAg in Fig. 3 at the equilibrium volume (a_0= 6.893 a.u.) and for a lattice constant reduction $1 - a/a_0 \simeq 8\%$. Comparison of Fig. 3 with analogous curves[15] for CeAg emphasizes the differences. For GdAg: (i) Δ_F is small and decreases slightly with pressure; (ii) the hybridization between f and conduction states becomes appreciably high with pressure only in the region of energy well above E_F, with no consequences on the Kondo effect.

In our opinion the comparison between CeAg and GdAg confirms the validity of the present approach to investigate theoretically actual f materials in a quantitative way.

We turn now to consider the Δ dependence on composition in order to see if the effect of electronic pressure is comparable to that of hydrostatic pressure. This is to separate the dependence of the s-f coupling on volume from that on electronic effects.

For the ternary alloys $\mathrm{CeCd}_{1-x}\mathrm{Zn}_x$, $\mathrm{CeAg}_{1-x}\mathrm{Zn}_x$, and $\mathrm{CeCd}_{1-x}\mathrm{Ag}_x$ an increase of x results in a volume decrease and one expects $\Delta(E_F)$ to increase accordingly.

The Slater-Koster parameters for the ternary compounds are obtained by linear interpolation of those fitted directly to the band structure of the pure compounds at equilibrium lattice constant. This is conceptually equivalent to considering a *virtual crystal* approximation for the crystal potential. We have tested the validity of this assumption by self-consistent FLAPW calculation for the alloy $\mathrm{Ce_2CdZn}$ with a cubic supercell of lattice constant $2a_0$ with four Cd, four Zn, and eight Ce per cell.[19]

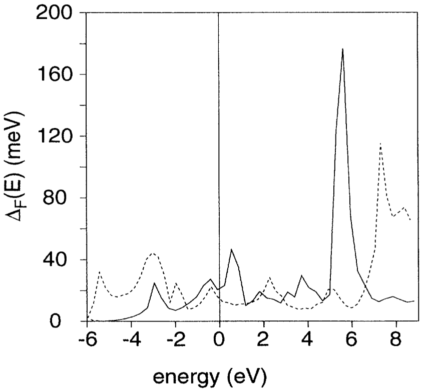

FIG. 3. Hybridization width calculated vs energy for GdAg in the atomic representation (N_Γ= 14) at equilibrium (solid line) and at reduced lattice constant $1 - a/a_0$= 7.9% (dashed line).

In Fig. 4 we plot $\Delta_F(x)$ normalized to $\Delta_F(0)$ for the three compounds as a function of x. It is possible to interpret this plot in terms of electronic pressure alone ignoring completely the influence of the possible electronic effect on Δ due to alloying. Let us therefore consider the variation of the lattice parameter $1 - a(x)/a_0$ with x, where $a(x)$ is obtained by linear interpolation of a_0 of the pure compounds. In this way the ordinate values in Fig. 4 may be compared directly with those in Fig. 2 for the abscissa value corresponding to $1 - a(x)/a_0$. One sees at once that the expected trend of increasing hybridization with decreasing volume cannot be applied *tout court* to alloys. In particular we find a reversed trend for $\mathrm{CeCd}_{1-x}\mathrm{Zn}_x$ and $\mathrm{CeAg}_{1-x}\mathrm{Zn}_x$, as observed experimentally in $\mathrm{U(Rh}_{1-x}\mathrm{Ru}_x\mathrm{)Si_2}$ (Ref. 10) and $\mathrm{Ce(Rh}_{1-x}\mathrm{Ru}_x\mathrm{)Si_2}$.[9] In the case of $\mathrm{CeCd}_{1-x}\mathrm{Ag}_x$, where the trend is positive, the increase of $\Delta(x)$ is, however, much larger than that reported in Fig. 2 at the corresponding lattice parameter.

From these observations it turns out that in alloys volume plays a minor role in driving Kondo-like magnetic instabilities compared to intrinsic electronic effects, especially in nonisovalent substitutional systems.

We summarize our conclusions as follows:

(i) It is possible to distinguish between a stable f and a Kondo-lattice system on the basis of our theoretical calculations of the hybridization width Δ in real materials. In fact our calculations show that $\Delta(E_F)$ is affected by pressure in CeCd, CeZn, and CeAg, while it is not in GdAg, which is a stable f-moment system.

(ii) Our calculations of Δ vs volume reduction allow

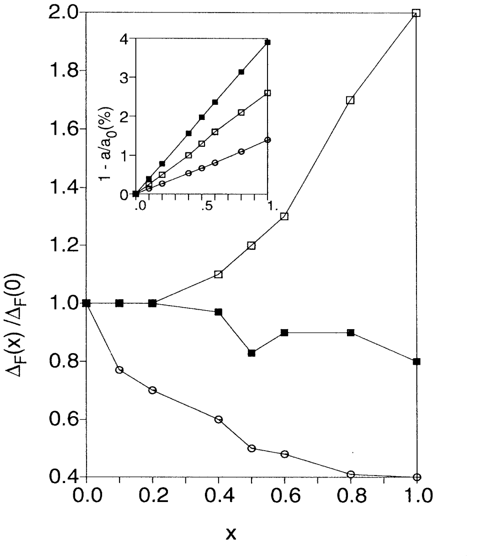

FIG. 4. Concentration dependence of the hybridization width at the Fermi energy $\Delta_F(x)$ normalized to $\Delta_F(0)$ for $\mathrm{CeCd}_{1-x}\mathrm{Ag}_x$ (empty squares), $\mathrm{CeCd}_{1-x}\mathrm{Zn}_x$ (full squares), $\mathrm{CeAg}_{1-x}\mathrm{Zn}_x$ (empty circles). The inset shows the percentual lattice constant reduction as a function of concentration x. $a(x)$ is obtained by linear interpolation from the a_0's of the pure compounds.

us to interpret the behavior of CeAg under pressure[11] in terms of the crossover from RKKY to the Kondo regime. Also CeZn and CeCd are likely to be moderate heavy-fermion systems according to the behavior of Δ vs volume.

(iii) Volume reduction, considered as a major cause of enhancement of the Kondo effect,[20] is presently found to play a minor role compared to intrinsic electronic effects in alloyed systems. The calculated behavior of Δ as a function of x in $\mathrm{CeAg}_{1-x}\mathrm{Zn}_x$ and $\mathrm{CeCd}_{1-x}\mathrm{Ag}_x$ may be qualitatively the same, which gives rise to the magnetic instability observed in $\mathrm{Ce(Rh}_{1-x}\mathrm{Ru}_x)\mathrm{Si}_2$ (Ref. 9) and $\mathrm{U(Rh}_{1-x}\mathrm{Ru}_x)\mathrm{Si}_2$.[10] Detailed calculations for the latter compound are in progress.

(iv) It would be interesting to check all our conclusions with further experimental data on these compounds. Measurements of the magnetic moment and T_C vs concentration in CeAg-Cd and CeAg-Zn systems would be of extreme importance to highlight point (iii). Moreover, measurements of the Grüneisen parameter of these compounds, not available so far, would also be very useful. In fact it has been shown recently that heavy-fermion compounds exhibit large values for such a parameter[21] that is also very sensitive to the volume dependence of the hybridization matrix element.[22]

ACKNOWLEDGMENTS

We wish to thank L.C. Andreani, A.K. McMahan, and P. Fazekas for helpful discussions. We acknowledge support by Computing facilities in Lausanne (Switzerland) (through Grant No. 20.28846.90 of the Swiss National Science Foundation) and by CINECA (Italy) (through a grant of the Consiglio Nazionale delle Ricerche).

---

[1] F. Steglich, U. Ahlheim, C.D. Bredl, C. Geibel, A. Grauel, M. Lang, G. Sparn, A. Krimmel, A. Loidl, and W. Assmus, J. Magn. Magn. Mater. **108**, 5 (1992); K. Bakker, A. de Visser, E. Brück, A.A. Menovsky, and J.J.M. Franse, *ibid.* **108**, 63 (1992), and references therein.

[2] T. Fujita, T. Suzuki, S. Nishigori, T. Takabatake, H. Fujii, and J. Sakurai, J. Magn. Magn. Mater. **108**, 35 (1992).

[3] J.C. Schrieffer and P. Wolff, Phys. Rev. Lett. **149**, 149 (1966).

[4] J. Kondo, Progr. Theor. Phys. **32**, 37 (1964).

[5] A ferromagnetic coupling of the Coulomb type may contribute to $J_{s\text{-}f}$. This is the source of the RKKY interaction in stable f-moment systems and does not give rise to a Kondo effect.

[6] P.W. Anderson, Phys. Rev. **124**, 41 (1961).

[7] S. Doniach, in *Valence Instabilities and Related Narrow Band Phenomena*, edited by R.D. Parks (Plenum, New York, 1977).

[8] J.S. Schilling, Adv. Phys. **28**, 657 (1979).

[9] B. Lloret *et al.*, J. Magn. Magn. Mater. **63&64**, 85 (1987).

[10] P. Burlet, F. Bourdarot, S. Quezel, J. Rossat-Mignod, P. Lejay, B. Chevalier, and H. Hickey, J. Magn. Magn. Mater. **108**, 102 (1992).

[11] A. Eiling and J.S. Schilling, Phys. Rev. Lett. **46**, 364 (1981).

[12] T. Shigeoka, Y. Uwakoto, H. Fujii, L. Rebelsky, S.M. Shapiro, and K. Asai, Phys. Rev. B **42**, 8394 (1990).

[13] H. Kadomatzu, M. Kurisu, T. Kitai, T. Okamoto, and H. Fujiwara, Phys. Lett. **94A**, 178 (1983).

[14] A. Continenza and P. Monachesi, Phys. Rev. B **46**, 6217 (1992).

[15] P. Monachesi, L.C. Andreani, A. Continenza, and A.K. McMahan, Appl. Phys. (to be published).

[16] H.F. Jansen and A.J. Freeman, Phys. Rev. B **30**, 561 (1984); U. von Barth and L. Hedin, J. Phys. **5**, 1629 (1972).

[17] P. Morin, J. Magn. Magn. Mater. **71**, 151 (1988).

[18] M. Croft *et al.*, Phys. Rev. Lett. **46**, 1104 (1981).

[19] P. Monachesi and A. Continenza, Nuovo Cimento D **15**, 307 (1993).

[20] J.W. Allen and R.M. Martin, Phys. Rev. Lett. **49**, 1106 (1982); L.Z. Liu *et al.*, Phys. Rev. B **45**, 8934 (1992).

[21] A. de Visser, J. Flouquet, J.J.M. Franse, P. Haen, K. Hasselbach, A. Lacerda, and L. Taillefer, Physica B **171**, 190 (1991).

[22] T.M. Hong, Phys. Rev. B **46**, 13 862 (1992).