

KKR-CPA study of the electronic and magnetic structures of disordered $\text{Pd}_{1-y}\text{Ni}_y$ alloys and their hydrides

M.G. Shelyapina^{a,b,*}, D. Fruchart^a, E.K. Hlil^a, S. Miraglia^a, D.S. dos Santos^{a,c}, S.S.M. Tavares^{a,d}, J. Toboła^{a,e}

^aLaboratoire de Cristallographie, CNRS, BP 166, 38042 Grenoble Cedex 9, France

^bInstitute of Physics, St. Petersburg State University, Ulyanovskaya 1, Petrodvorets, St. Petersburg 198904, Russia

^cCOPPE/UFFRJ, C.P. 68505, 21945-970 Rio de Janeiro, RJ, Brazil

^dDepartamento de Eng. Mecânica/UFF, R. Passo da Patria 156, 24210-470 CEP, Brazil

^eFaculty of Physics and Nuclear Techniques, AGH, Al. Mickiewicza 30, 30-059 Kraków, Poland

Received 1 September 2002; accepted 15 October 2002

Abstract

The electronic and magnetic structures of $\text{Pd}_{1-y}\text{Ni}_y$ alloys were calculated using the charge and spin self-consistent Korringa–Kohn–Rostoker method combined with the coherent potential approximation (KKR-CPA). The total and atomic magnetic moments were estimated versus y , the nickel concentration. For $0.01 \leq y \leq 0.1$ and $0.5 \leq y \leq 0.99$, the magnetic moment of Ni does not vary, being respectively 0.44 and $0.69 \mu_B/\text{f.u.}$, and for intermediate compositions it increases linearly with y . For several Ni contents, the total and atomic magnetic moments were calculated versus x for $\text{Pd}_{1-y}\text{Ni}_y\text{H}_x$ and then compared with other theoretical and experimental data. © 2003 Elsevier B.V. All rights reserved.

Keywords: PdNi alloys; Metal hydrides; Electronic structure calculations

1. Introduction

Metal–hydrogen systems have attracted much attention during the last decade from both an experimental and theoretical viewpoint. Hydrogen inserted in a metal can dramatically change the fundamental properties of the host matrix. For example, Pd, a near-ferromagnetic metal, yields superconducting PdH_x at low temperature when hydrogenated. The ferromagnetic properties of NiH_x vanish when the hydrogen concentration is increased. In this system, theoretical calculations of the electronic states versus $x(\text{H})$ were performed on the basis of the linear-muffin-tin-orbital (LMTO) formalism (e.g. Ref. [1]). Since it was assumed that the H vacancies are ordered, only a limited number of x values were probed due to symmetry limits. For a more realistic approach, a random repartition of H in each of the interstitial sites should be accounted

for, using, for example, the coherent-potential-approximation method. Similarly, the electronic structure of PdH_x has been carefully investigated. The main effect of H insertion is to create bonding states below the Pd d band (see, for example, Ref. [2] and references therein). In addition, Pd-based binary alloys are very interesting due to the giant magnetic moment induced by Pd at the 3d transition metal impurity site [3], such as, for example, $8 \mu_B$ for Mn, $12.6 \mu_B$ for Fe, and $10.8 \mu_B$ for Co [4]. Theoretical analyses of the induced magnetization on 3d transition metal impurities in Pd show that the 3d–Pd interaction decreases from Cr to Ni [5].

Therefore, it would be interesting to study the impact of hydrogen insertion on the magnetization of 3d impurities in Pd–3d–H systems. We present here a theoretical KKR-CPA analysis of the electronic and magnetic structures of disordered $\text{Pd}_{1-y}\text{Ni}_y$ alloys and their hydrides $\text{Pd}_{1-y}\text{Ni}_y\text{H}_x$ versus the Ni and H concentrations. The total and partial densities of states (DOSS) were calculated at each atom site as well as the angular momentum decomposition and the total and atomic magnetic moments.

*Corresponding author. Institute of Physics, St. Petersburg State University, Ulyanovskaya 1, Petrodvorets, St. Petersburg 198904, Russia.
E-mail address: phys@ms4828.spbu.edu (M.G. Shelyapina).

2. Method of calculation

The charge and spin self-consistent Korringa–Kohn–Rostoker coherent-potential-approximation (KKR-CPA) method [6,7] was used for the electronic and magnetic structure analysis of $\text{Pd}_{1-y}\text{Ni}_y$ alloys and hydrides. The exchange-correlation effects are accounted for within the von Barth–Hedin local spin density approximation [8]. The electron charge density and the crystal potential are assumed to be spherically symmetrical within muffin-tin (MT) spheres, and constant in the interstitial region. The Pd (Ni) hydride has a rock-salt structure where hydrogen atoms occupy all the octahedral sites of the f.c.c. metal lattice [9,10]. The cell parameter of the NiH_x hydride, a_{NiH_x} , can be expressed by [9]

$$a_{\text{NiH}_x} = (a_{\text{Ni}}^3 + 4x \cdot \Delta V_{\text{H}})^{1/3} \quad (1)$$

where a_{Ni} represents the cell parameter of pure Ni, and ΔV_{H} , the experimental volume expansion coefficient for H in Ni, is $2.8 \text{ \AA}^3/\text{H atom}$ [10]. Applied to PdH_x , one finds a

ΔV_{H} value of $2.24 \text{ \AA}^3/\text{H atom}$. Because of the paucity of data for both the cell parameters of $\text{Pd}_{1-y}\text{Ni}_y$ and their hydride, we assumed that the lattice constant varied linearly with y when extrapolated from the values of 3.5332, 3.87 and 4.06 \AA for Ni, Pd [11] and PdH, respectively [12,13]. The radii of the MT spheres were chosen so as not to overlap, and to improve, the fits of the Wigner–Seitz volume for all y or x ranges. The total, site and l -decomposed DOSs were computed for the final potential converging up to 1 mRy, accounting for the s-, p- and d-valence states.

3. Results and discussion

3.1. $\text{Pd}_{1-y}\text{Ni}_y$ alloy

The total DOSs in $\text{Pd}_{1-y}\text{Ni}_y$, $y=0.01, 0.4, 0.6$ and 0.99 , are plotted in Fig. 1a–d. The major (up) and minor (down) total DOSs in $\text{Pd}_{0.99}\text{Ni}_{0.01}$ exhibit very similar shapes (Fig. 1a), although the minor spin band appears to have a somewhat greater width. Hence, very little Ni impurity effects ferromagnetism in $\text{Pd}_{1-y}\text{Ni}_y$. For further substitutions of Ni for Pd ($y=0.4$), changes appear in the DOS, being minor in the up-spin region and significant in the down-spin region (Fig. 1b). The DOS shape is smoothed, reflecting a disordered smearing of states: the sharp peak at 0.42 Ry for $\text{Pd}_{0.99}\text{Ni}_{0.01}$ is not observed for $\text{Pd}_{0.6}\text{Ni}_{0.4}$. The up- and down-spin parts are not symmetrical, and the down-spin DOS is shifted to higher energies. As can be seen in Fig. 1c, $\text{Pd}_{0.4}\text{Ni}_{0.6}$ shows a similar DOS with little change. However, the situation with $\text{Pd}_{0.01}\text{Ni}_{0.99}$ is quite different (Fig. 1d). The DOS is more localized and symmetrical, and is very close to that of pure Ni obtained with the KKR and KKR-CPA methods [14].

These results give an insight into how magnetic moments form on Pd and Ni atoms. Pure Pd is non-magnetic; however, Ni impurities induce a magnetic moment on Pd. The s, p and d contributions to the DOS at the Pd and Ni atoms in $\text{Pd}_{1-y}\text{Ni}_y$ ($y=0.01, 0.4$ and 0.99) were calculated and the results for $y=0.01$ are shown in Fig. 2. For small Ni contents y , the up-spin d band is filled in the Ni DOS and partly filled in the Pd DOS. For down spin, the high-energy peaks in both the Pd and Ni DOSs are partly empty. With increasing y , the up-spin d band of Pd fills, while the down-spin d bands for both atoms become essentially empty.

It is assumed that spin polarization occurs for the d states. For the smallest Ni content ($y=0.01$, Fig. 2), the Ni d band for both spin directions can be decomposed into a large band of low density and a narrow band of high density. The appearance of this peak results from the strong hybridization of the impurity d electrons with the host d electrons. As for the s and p Ni states, they contribute poorly to the spin polarization, which is caused by the interaction with neighboring Pd atoms, which are

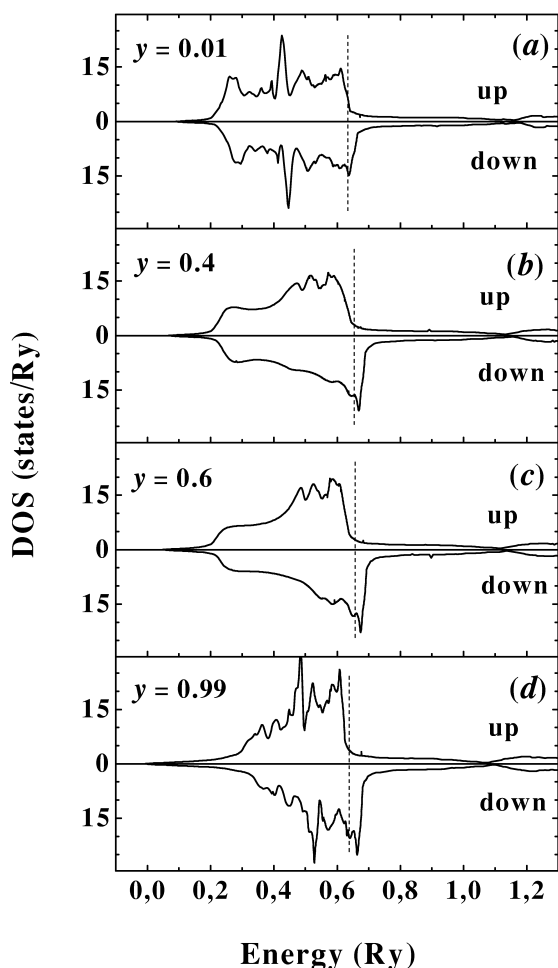


Fig. 1. Self-consistent KKR-CPA total DOS in disordered $\text{Pd}_{1-y}\text{Ni}_y$ alloys with $y=0.01$ (a), $y=0.4$ (b), $y=0.6$ (c), and $y=0.99$ (d). Dashed vertical lines denote the Fermi energy, E_{F} .

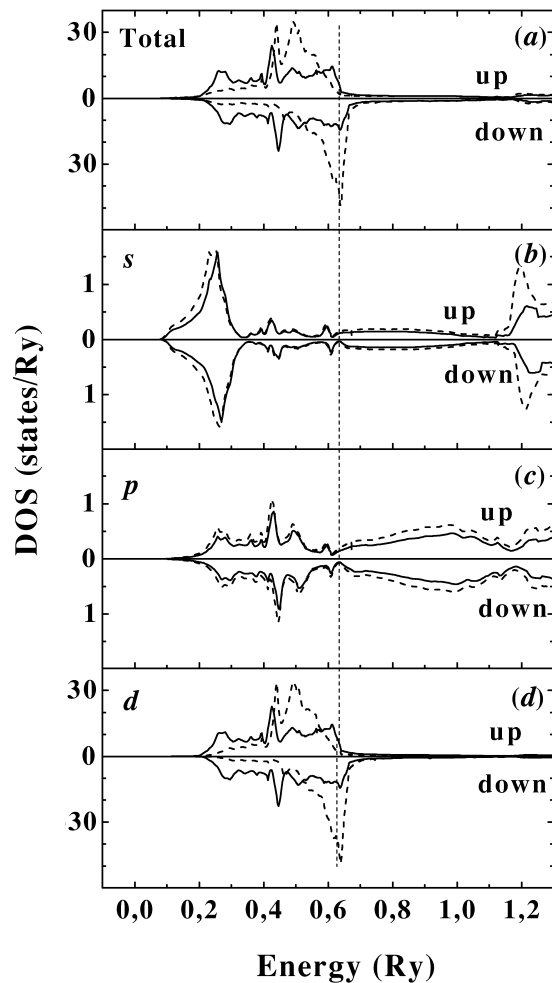


Fig. 2. Site-dependent KKR-CPA DOS in $\text{Pd}_{0.99}\text{Ni}_{0.01}$. The Pd and Ni components are shown by solid and dashed lines, respectively. The total DOSs associated with Pd and Ni as well as the l -decomposed DOS are shown.

also magnetically polarized. As reported previously [15], the gap in the s and p states of 3d metals comes from their interaction with the Pd 4d band. Such a trend is common

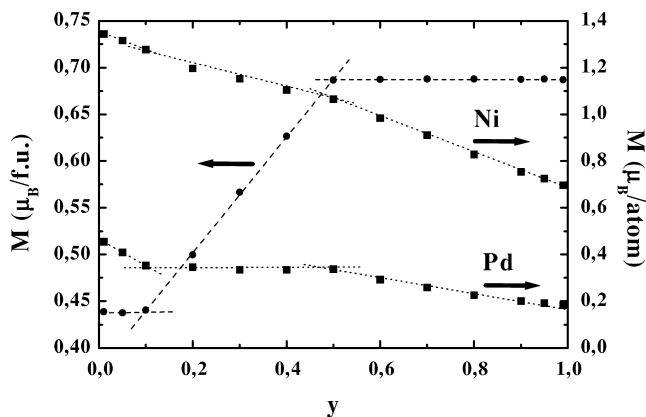


Fig. 3. Calculated values of the total and atomic magnetic moments for $\text{Pd}_{1-y}\text{Ni}_y$ versus Ni content y .

for magnetic 3d impurities in noble metals [15–17]. For larger Ni contents, the high-intensity peak in the Ni d states and the gaps in the s and p states both disappear as a result of the reduced polarization at the Pd site.

Fig. 3 shows the total magnetic moment and its components for $\text{Pd}_{1-y}\text{Ni}_y$ plotted versus y . There are three different states for the total magnetic moment behavior. For $0.01 \leq y \leq 0.1$ and $0.5 \leq y \leq 0.99$ the magnetic moment does not vary, being 0.44 and 0.69 $\mu_B/\text{f.u.}$, respectively, but in the intermediate range it increases linearly with y . In contrast to the total moment, the atomic magnetic moments are maximum for the smallest Ni concentration, for Ni and Pd as well, and are equal to 1.34 and 0.46 μ_B , respectively. As can be seen from Fig. 3, the magnetic moment of Ni decreases linearly up to 0.7 μ_B for $y=0.99$, when the Ni content increases. In addition, the magnetic moment of Pd also decreases; however, it does not change within the range $0.1 < y < 0.5$.

3.2. $\text{Pd}_{1-y}\text{Ni}_y$ hydride

The total DOSs in $\text{Pd}_{0.4}\text{Ni}_{0.6}\text{H}_x$ for $x=0, 0.3$ are 0.7 are plotted in Fig. 4. Clearly, $\text{Pd}_{0.4}\text{Ni}_{0.6}$ appears magnetically ordered. The up and down total DOSs exhibit quite different shapes: the minor spin band is smoother and has a markedly greater width than that of the major spin band, as seen in Fig. 4a. It is worth noting that, reflecting the disordered smearing of states, in $\text{Pd}_{1-y}\text{Ni}_y$ the DOS shape is generally softened in comparison with the case for pure Pd or Ni. As shown in Fig. 4b and c, hydrogen insertion leads to noticeable changes in the total DOS. General trends can be observed: first, the large band close to 0.1 Ry becomes increasingly larger when the H content is increased; the up-spin part is then smoother in the hydride, having a shape similar to that of the down-spin part. The sharp peak found near the Fermi level (E_F) in the down-spin part of the DOS of $\text{Pd}_{0.4}\text{Ni}_{0.6}$ also appears in the up-spin part of the hydride. Finally, the width of the down-spin band decreases in a such manner that, for $x=0.7$, it is essentially filled. The more localized DOS situation is similar to that found in NiH_x [1], as calculated for several H contents when the hydrogen vacancies were assumed ordered. In $\text{Pd}_{0.4}\text{Ni}_{0.6}\text{H}_x$ ($x=0.0, 0.3$ and 0.7) the s , p and d contributions to the DOS at the Pd and Ni sites were also derived. For $x=0$ the l -decomposed DOSs reveal the same trends for both atoms: the up-spin d bands are filled, and for the down spins, the high-energy peak is partly empty. When x increases to 0.3, the down-spin d bands of both Pd and Ni are filled, while for both atoms the up-spin d bands do not change. For $x=0.7$, the down-spin d band of Pd is almost filled, in contrast to that of Ni, which remains almost empty. In $\text{Pd}_{0.4}\text{Ni}_{0.6}\text{H}_{0.3}$ and $\text{Pd}_{0.4}\text{Ni}_{0.6}\text{H}_{0.7}$, the H s DOS exhibits a large peak between 0 and 0.2 Ry. Such a peak appears in all the Pd and Ni DOS components, but it is more marked for the Pd s , p , d

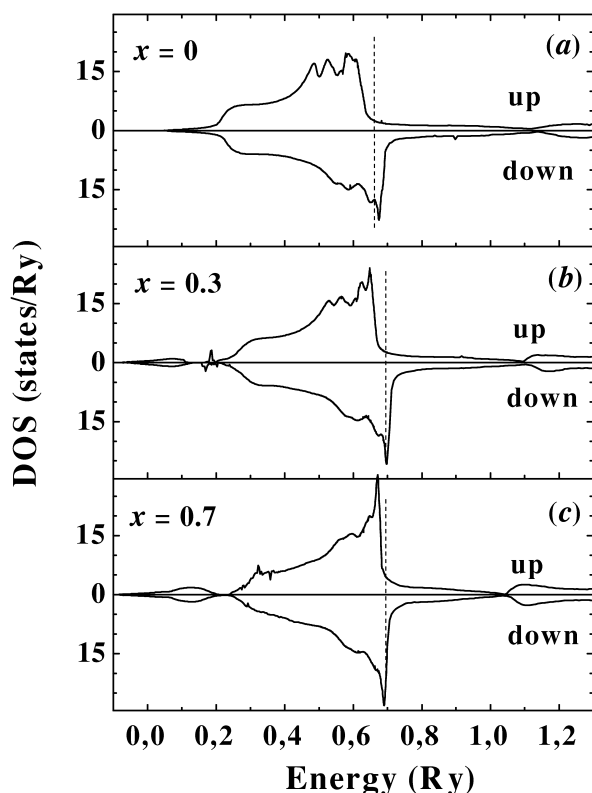


Fig. 4. Self-consistent KKR-CPA total DOS in disordered $\text{Pd}_{0.4}\text{Ni}_{0.6}\text{H}_x$ alloys: $x = 0$ (a), $x = 0.3$ (b), and $x = 0.7$ (c). Dashed vertical lines denote the Fermi energy, E_F .

and Ni s, p bands, because of the large hybridization with those bands.

As is well known, the ferromagnetic character of Ni is strongly affected by the insertion of hydrogen, and palladium hydride exhibits superconducting properties. Thus, analysis of the impact of H insertion on the magnetic properties of Pd–Ni alloys would be interesting. In the $\text{Pd}_{1-y}\text{Ni}_y\text{H}_x$ system, the total magnetic moment and its components were determined for several Ni contents, namely $y = 0.4, 0.6$ and 1 , as shown in Fig. 5. Fig. 5a shows that the total magnetic moment does not depend merely on y , as observed for $\text{Pd}_{1-y}\text{Ni}_y$; e.g. for $x = 0.01$ it is equal to about $0.67 \mu_B/\text{f.u.}$ When x increases it decreases linearly to 0 for $x = 0.9$. This critical value is close to the $0.58 \mu_B/\text{f.u.}$ measured experimentally for NiH_x [18]. For Ni, the dependence of the experimental magnetic moment on the H content is shown in Fig. 5a by the dashed line. It varies linearly in the range $x = 0-0.6$ and is 0 for $x > 0.6$, opposite to the case for the total magnetic moment, which strongly depends on the Ni concentration. For x values up to 0.8, the magnetic moment at both sites decreases with increasing y , as seen from Fig. 5b. For $x = 0.01$, when hydrogen may be considered as an impurity, the Ni magnetic moment is calculated to be $1.12, 0.97$ and $0.7 \mu_B$ for $y = 0.4, 0.6$ and 1 , respectively; it then decreases to about $0.1 \mu_B$ at $x = 0.9$

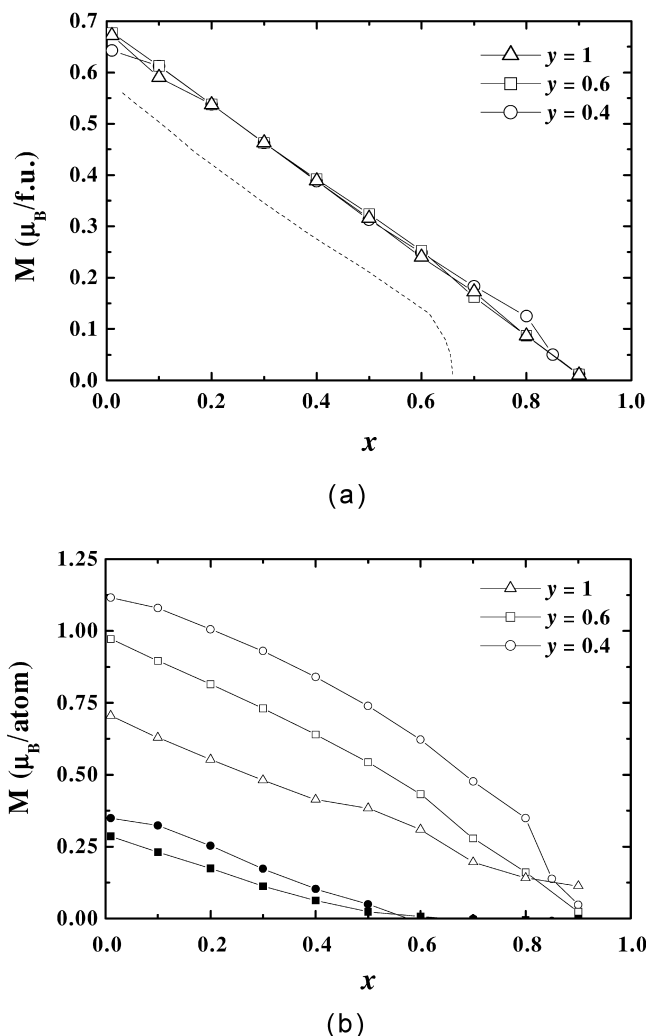


Fig. 5. Calculated values of the total (a) and atomic (b) magnetic moments in $\text{Pd}_{1-y}\text{Ni}_y\text{H}_x$ for $y = 0.4, 0.6$ and 1 versus the H content x . (a) Experimental data from Ref. [18] are represented by the dashed line for NiH_x . (b) Open and filled symbols correspond to the magnetic moment values calculated at the Ni and Pd sites, respectively.

for all Ni concentrations. Conversely, for $x = 0.01$, Pd exhibits a larger magnetic moment of 0.35 and $0.29 \mu_B$ for $y = 0.4$ and 0.6 , respectively; it is found to be non-magnetic for $x = 0.6$.

4. Conclusion

KKR-CPA calculations show unexpected behavior of the atomic and total magnetic moments in the disordered alloy $\text{Pd}_{1-y}\text{Ni}_y$. Hydrogen insertion leads to noticeable changes in the magnetic moment of both atoms. For example, for the smallest hydrogen content x , the total moment does not depend on y . When x increases in $\text{Pd}_{1-y}\text{Ni}_y\text{H}_x$, the atomic magnetic moments decrease to 0, but different, critical x values are found, which are equal to 0.6 and 0.9 for the Pd and Ni atoms, respectively.

Acknowledgements

MGS was supported during her stay by the Université J. Fourier, Grenoble, through a grant from the 'Rhône-Alpes' action TEMPRA, which also sponsors the cooperation between Grenoble and Cracow (JT).

References

- [1] P. Vargas, N.E. Christensen, Phys. Rev. B 35 (1987) 1993.
- [2] C.T. Chan, S.G. Louie, Phys. Rev. B 27 (1983) 3325.
- [3] F.W. Constant, Phys. Rev. B 36 (1930) 1654.
- [4] G.J. Nieuwenhuys, Adv. Phys. 24 (1975) 515.
- [5] J.F. van Acker, W. Speier, R. Zeller, Phys. Rev. B 43 (1991) 9558.
- [6] S. Kaprzyk, A. Bansil, Phys. Rev. B 42 (1990) 7358.
- [7] A. Bansil, S. Kaprzyk, Phys. Rev. B 43 (1991) 10335.
- [8] U. von Barth, L. Hedin, J. Phys. C 5 (1972) 1629.
- [9] See, e.g., H. Peisl, in: G. Alefeld, J. Volkl (Eds.), Hydrogen in Metals, Vol. I, Springer, Berlin, 1978.
- [10] X.W. Lin, M.O. Rouault, A. Traverse, J. Chaumont, M. Salomé, H. Bernas, Phys. Rev. Lett. 56 (1986) 1835.
- [11] P. Villars, L.D. Calvert (Eds.), Pearson's Handbook of Crystallography Data for Intermetallic Phases, Vol. 3, AMS, 1985.
- [12] X.W. Wang, S.G. Louie, M.L. Cohen, Phys. Rev. B 40 (1989) 5822.
- [13] C.T. Chan, S.G. Louie, Phys. Rev. B 27 (1983) 3325.
- [14] A. Bansil, S. Kaprzyk, A. Andrejczuk, L. Dobrzynski, J. Kwiatkowska, F. Maniawski, E. Zukrowski, Phys. Rev. B 57 (1998) 314.
- [15] P.J. Braspenning, R. Zeller, A. Lodder, P.H. Dederichs, Phys. Rev. B 29 (1984) 703.
- [16] R. Zeller, R. Podloucky, P.H. Dederichs, Z. Phys. B 38 (1980) 165.
- [17] R. Podloucky, R. Zeller, P.H. Dederichs, Phys. Rev. B 22 (1980) 577.
- [18] H.J. Bauer, E. Schmidbauer, Z. Phys. 164 (1961) 367.