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The effect of structural vacancies and substitutional impurities on the electronic and magnetic properties of cobalt, nickel, copper and palladium monohydrides

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Abstract. Using the self-consistent LMTO Green function method, band-structure calculations have been carried out for CoH, NiH, CuH and PdH containing single defects such as lattice vacancies and substitutional d-metal impurities. The nature of the formation of electronic states and inter-atomic bonds in non-stoichiometric and ternary alloys based on monohydrides is analysed. The change in the sum of one-electron energies caused by the formation of metallic and H vacancies and during the dissolution of 3d and 4d metals has been evaluated. The estimates are used for discussing the relative stability of ternary hydride alloys.

A general model of the energy spectrum of 3d and 4d impurities in cubic monohydrides is proposed. On the basis of calculations, an analysis is made of the applicability of the phenomenological rigid-band model to describing the energy spectrum of polycrystalline dilute hydride alloys.

1. Introduction

Previous papers (Ivanovsky *et al* 1987a, 1988a, b, Ivanovsky and Gubanov 1988, Anisimov *et al* 1988) have provided LMTO Green function (LMTO GF) band calculations of the electronic states of cubic refractory phases (3d- and 4d-element carbides, nitrides and oxides) that contain metallic and non-metallic vacancies and also substitutional impurities represented by Be, B, C, N, O and all 3d and 4d elements. The computations performed permitted ascertaining the major features peculiar to the formation of local densities of states (LDOS) of defects and determining the influence of defects on the electronic properties of initial binary phases.

Equally well known is the effect of structural defects on the transition-metal hydrides. Doping hydride sublattices with different elements (or 'doping' these sublattices with vacancies) affords ample opportunities of modifying their physicochemical, structural and many other properties (see, e.g., Alefeld and Völkl 1978).

Currently, the band structures of many binary ordered hydrides have been well studied in terms of various computational techniques of solid state physics (see the reviews by Switendick (1978) and Ivanovsky *et al* (1987b)). Among the disordered hydride phases, sufficiently full study has been made of the non-stoichiometric Y, Ce, Ti and Zr trihydrides and dihydrides and Pd monohydride (see the reviews by Bansil *et al* (1983) and Ivanovsky *et al* (1987b)). Far less information is available on the electronic

properties of hydrides doped with different impurities. Therefore, in interpreting experimental data for dilute ternary (and more complicated) alloys, the LDOS of impurities are often approximated by the Lorentz function (according to the concept of a virtual bound state (Friedel 1958, Alexander and Andersen 1964)). For concentrated systems a qualitative rigid-band model is used (see, e.g., Wike and Brodovsky 1978).

Numerical computations are available only for alloys of PdH with some noble metals (Papaconstantopoulos *et al* 1979, Temmerman and Pindor 1983, Pindor *et al* 1983), for TiH₂ and ZrH₂ doped with all 3d and 4d metals (Ivanovsky and Gubanov 1988), and for the concentration dependences of the DOS in the cubic systems Ti–V–H and Ti–Nb–H (Papaconstantopoulos and Laufer 1987). An overview of theoretical papers dealing with the study of the electronic spectra of intermetallic hydrides (TiFe, LaNi₅, NiMg₂, etc) is provided in a monograph by Ivanovsky *et al* (1987b).

The electronic and magnetic properties of dilute solid solutions (sss) based on cubic (B1-type) transition-metal hydrides undergo changes that result from the dissolution of impurity atoms (or from the vacancy 'dissolution') in the bulk of the matrix.

The purpose of the present paper is to study the general tendencies in the alteration of these properties. To this end, *ab initio* band calculations of single 3d and 4d metal atoms in CoH, NiH, CuH and PdH have been carried out. Choosing the initial hydrides enables one to trace features peculiar to the formation of defect LDOS in a series of isostructural phases that exhibit similar electronic spectra but differ in valence electron concentrations (valence band occupancies). For CoH and CuH the LDOS of single H vacancies have also been calculated, and for NiH the LDOS of the H and metallic (M) vacancies have been estimated. The magnetic characteristics of the impurity 3d and 4d centres in PdH are discussed on the basis of spin-polarised calculations.

2. Computational aspects

The electronic structure of complete monohydrides as well as of single H and M vacancies and 3d and 4d impurities therein was calculated using a self-consistent LMTO GF method (Gunnarsson *et al* 1983, Koenig *et al* 1986).

The description of the computation algorithm used has been presented in more detail by Anisimov *et al* (1988) and Ivanovsky *et al* (1988a). The lattice spacing values used for CoH, NiH and CuH are those obtained in augmented spherical-wave calculations of these monohydrides (Williams *et al* 1979), and the values used for PdH are those given by Goldschmidt (1967). The possible lattice relaxations in the present calculations for the defect systems were neglected.

3. Results and discussion

3.1. Ideal binary monohydrides

The total densities of states (TDOS) for the complete cubic CoH, NiH and CuH are presented in figure 1, and some electronic parameters are given in table 1. As can be seen, the TDOS of the hydrides differ dramatically from those of the initial metals (Moruzzi *et al* 1978) and are characterised by the presence of two valence subbands. Note that, although no new bands arise during the formation of hydrides (compared with pure metals), the lower metallic s, d-type band undergoes severe deformation (accompanied by a decrease in energy) owing to its hybridisation with H wavefunctions,

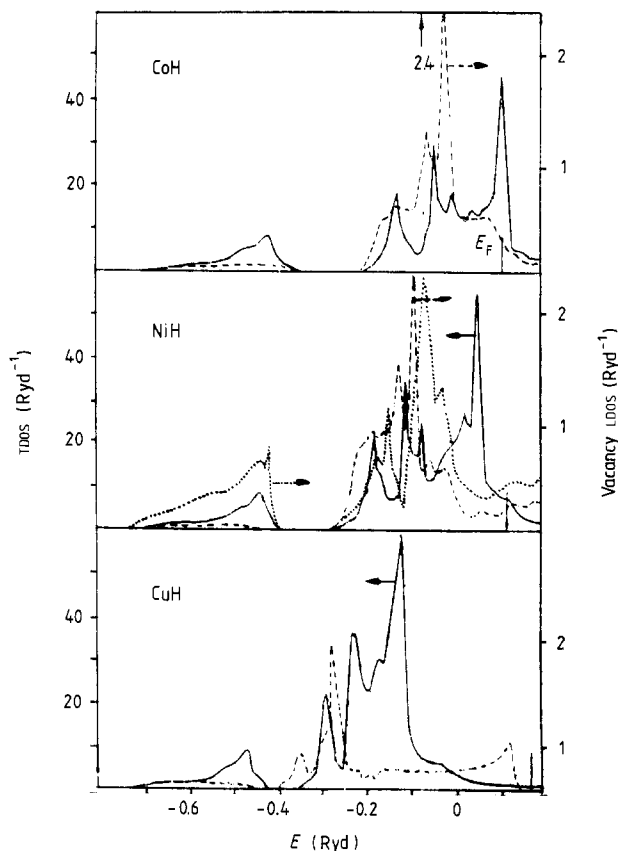


Figure 1. TDOS of B1 monohydrides of Co, Ni and Cu (—) and LDOS of single H (---) and Ni (····) vacancies in these compounds.

a fact which gives rise to a well defined low-energy TDOS structure. In addition to the H 1s states, participants in the formation of this mixed subband are also s, p, d metallic orbitals (table 1). The band adjacent to the Fermi level is constituted chiefly by d functions of the metal with minor admixtures of s, p as well as H 1s states. The relative positions of the above bands is determined by the degree of hybridisation of atomic valence states in the alloys and decreases appreciably on going to CuH.

The Fermi level position depends on the valence electron concentration (VEC) of the hydride. For CoH (VEC = 10), E_F is located at the top of the filled band and coincides with the intensive TDOS resonance (figure 1). This indicates, on the one hand, the

Table 1. Constitution of the valence bands of CoH, NiH and CuH.

	H 1s-M d, s, p				M d, s, p			
	H 1s	M s	M p	M d	H 1s	M s	M p	M d
CoH	0.788	0.359	0.420	0.388	0.036	0.171	0.322	7.340
NiH	0.769	0.347	0.416	0.380	0.065	0.191	0.314	8.352
($a = 7.1$ au)								
CuH	0.703	0.411	0.414	0.460	0.159	0.143	0.446	9.126

electronic nature of the structural instability in complete CoH and leads also to spin-polarisation effects in the system. Thus, the value of the local moment of Co in $\text{CoH}_{1.0}$ according to estimates (Alekseev *et al* 1987) is between $1.12\mu_B$ and $1.16\mu_B$. For NiH (VEC = 11) the d band of Ni turns out to be filled, and $N^{\text{NiH}}(E_F) \ll N^{\text{CoH}}(E_F)$ (figure 1). Note at once that, according to our estimates (see also Kulikov 1979, Papaconstantopoulos 1981, Switendick 1978, 1979), $N(E_F)$ and the energy interval between H 1s and d, s-like sub-bands for isoelectronic PdH are somewhat smaller than the counterparts for NiH.

For the example of NiH, we investigated also the dependence of the electronic structure parameters of hydrides on the magnitude of the lattice spacing, since no unambiguous data are available on the structure parameters of strictly stoichiometric cubic CoH, NiH and CuH. The results obtained over the range $a_{\text{NiH}} = 7.0\text{--}7.1$ au with a step of 0.02 au show that, as a_{NiH} is decreased, the energy interval between the centres of the binding H 1s and Ni d, s sub-bands increases by about 0.15 Ryd, thereby reflecting enhancement of the hybridisation of binding states for the 'compressed' hydride. In this case, $N(E_F)$ decreases slightly (by about 1%). In addition, the relative contributions to $N(E_F)$ by individual states, among which Ni 3d states dominate, remain almost stable.

Finally, for CuH (VEC = 12), E_F lies beyond the d band (figure 1); so the instability of cubic CuH (which under equilibrium conditions has a hexagonal structure) may qualitatively be attributed to an abrupt increase in the system's one-electron energy (relative to the stable NiH) as an extra electron is introduced (see also Williams *et al* 1979).

3.2. Lattice vacancies

A further step in our research was to study the effect of H and M vacancies on the band structure of monohydrides. Figure 1 presents LDOS of single H defects in the region of metallic sub-bands of the hosts (CoH, NiH and CuH) with maxima that coincide in energy with the host's local DOS minima.

For the hydrides and isostructural carbides, nitrides and oxides, a profound analogy in the formation of the vacancy LDOS structure (Marksteiner *et al* 1986a, b, Redinger *et al* 1985, 1986, Ivanovsky *et al* 1987a, 1988a, b) may be noted here which is due to the same physical mechanism of the readjustment of electronic states in a crystal as vacancies are introduced. In both cases the vacancy states concentrate near the lower edge of the occupied metallic band, reflecting the 'capture' of the states of the nearest metallic octahedron (in B1 structure) by the defect sphere. As this occurs, the breaking of a number of M–H bonds is responsible for the energy readjustment of the aforementioned states, when the lower metallic band (earlier hybridised with H 1s functions) suffer 'reverse deformation' and moves to E_F , as indicated by the shape of the LDOS of the 'vacancy' functions that hybridise with this band. Note that the 'reverse-deformation' energy, which may be correlated with the energy position of the vacancy band maximum in the spectrum of the hydride, can qualitatively specify the degree of M–H bonding in different MH phases. As is then manifest from figure 1, such interactions are the weakest in CuH (see also below).

Let it be also emphasised that the contributions by the LDOS of H vacancies to the region of the H 1s-like band are extremely small, a fact which indicates the local character of the H states that enter into short-range interactions with the neighbouring metallic centres.

The LDOS of the metallic vacancy in NiH has a different shape (figure 1) and form two well defined bands that lie inside the ranges of the H 1s- and Ni d, s-like bands of

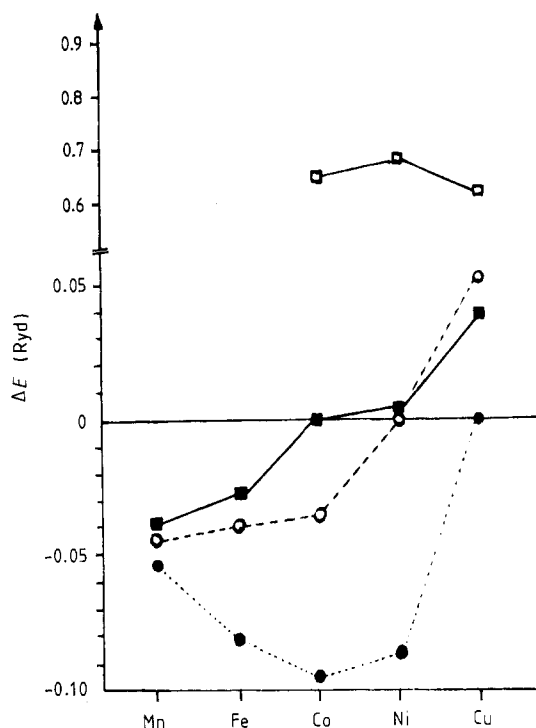


Figure 2. Values of ΔE for H vacancies in CoH, NiH and CuH (□), for the Ni vacancy in NiH(*) and for single impurities of some 3d metals in CoH (■), NiH (○) and CuH (●).

the hydride. It may be asserted that the LDOS of the Ni defect forms, just as in the case of a H vacancy, owing to hybridisation of effective 'vacancy' functions with states of the crystalline environment.

Therefore, if single H vacancies have a sufficiently local perturbing effect, restricted to the nearest crystalline environment, on the energy spectrum of the hydride, then the emergence of an M vacancy will lead to a far more dramatic influence on the electronic states of the crystal by causing the DOS of the matrix to readjust over the entire range of the valence spectrum.

A general idea of the energy effects that accompany the formation of crystal vacancy is given by the quantities ΔE (which characterised the one-electron energy change of the surrounding crystal as a single defect is injected (Ivanovsky *et al* 1988a), and these are presented in figure 2. Inspection of this figure shows that $\Delta E_{\text{NiH}}^{\text{vac}}(\text{Ni}) > \Delta E_{\text{NiH}}^{\text{vac}}(\text{H})$; for hydrides, therefore, vacancies are most likely to form in the H sublattice. Conversely, formation of M vacancies (with respect to the metal) is not expected in these systems, by contrast with, for example, a number of oxide phases (Goldschmidt 1967). On the contrary, ΔE for H vacancies is maximal in NiH (strongest M–H bond) and minimal in CuH; this correlates with the stability of the cubic hydride phases of these metals.

3.3. Substitutional metal impurities

We proceed to consider another type of imperfect system, i.e. CoH, NiH and CuH containing the substitutional impurities Mn, Fe, Co, Ni and Cu atoms. The LDOS of the impurities involved (spin-restricted calculations) are given in figure 3, and some of their electronic and energy characteristics in figure 2 and table 2.

It is seen that the shape of the impurity LDOS (ILDOS) differ drastically from the Lorentzian shape and feature considerable hybridisation of the impurity states with the

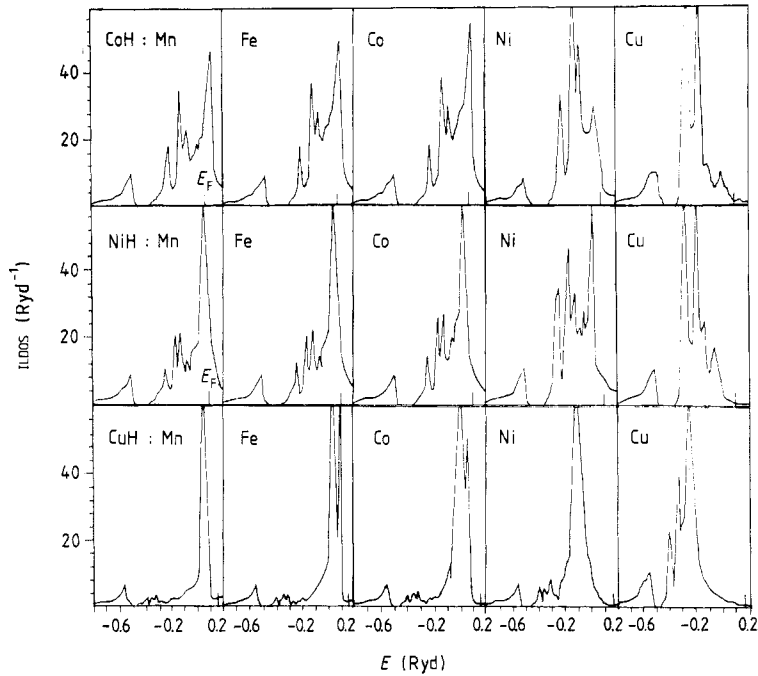


Figure 3. ILDOSS of some 3d impurities in CoH, NiH and CuH.

Table 2. Parameters of the electronic structure of crystal defects in CoH, NiH and CuH.

Hydride	Defect	R^{imp} (au)	$\Delta N^{imp}(E_F)$ (Ryd ⁻¹)	$N^{imp}(E_F)$ (Ryd ⁻¹)	$N^{1(imp)}(E_F)$ (Ryd ⁻¹)			Centres of filled impurity bands (Ryd)		
					s	p	d	s	p	d
CoH	Mn	2.579	0.20	32.450	0.056	0.332	32.062	0.485	0.343	0.084
CoH	Fe	2.584	0.35	25.453	0.050	0.302	25.101	0.491	0.348	0.095
CoH	Ni	2.608	9.01	17.239	0.045	0.212	16.982	0.506	0.349	0.100
CoH	Cu	2.617	7.80	3.248	0.052	0.268	2.928	0.529	0.359	0.221
NiH	Mn	2.510	-2.97	44.024	0.088	0.532	43.404	0.500	0.365	0.069
NiH	Fe	2.512	-2.80	38.580	0.094	0.552	37.934	0.507	0.367	0.090
NiH	Co	2.530	-1.53	20.934	0.104	0.608	20.222	0.517	0.371	0.114
NiH	Cu	2.648	1.35	2.656	0.140	0.848	1.668	0.542	0.379	0.219
CuH	Mn	2.450	-2.38	4.199	0.001	0.009	4.189	0.567	0.394	-0.020
CuH	Fe	2.431	-0.52	2.107	0.001	0.006	2.100	0.574	0.399	-0.005
CuH	Co	2.427	0.05	1.328	0.001	0.001	1.326	0.581	0.400	0.037
CuH	Ni	2.485	0.04	0.166	0.001	0.012	0.144	0.591	0.402	0.132

valence orbitals of the matrix. As a result, the ILDOSS, just as the LDOS of Co, Ni and Cu in the monohydrides (also shown in figure 3), acquire a clearly marked two-band structure, testifying to an admixture of impurity states in both H 1s- and M d, s-like bands of hydrides. As follows from figure 3, the shape of the ILDOS depends on the species of metal introduced and on the band structure of the matrix. Thus, as the atomic number of the impurity is increased (Mn → Cu), the orbital energies of external states rise systematically (most appreciably for d orbitals; see table 2) and the impurity band

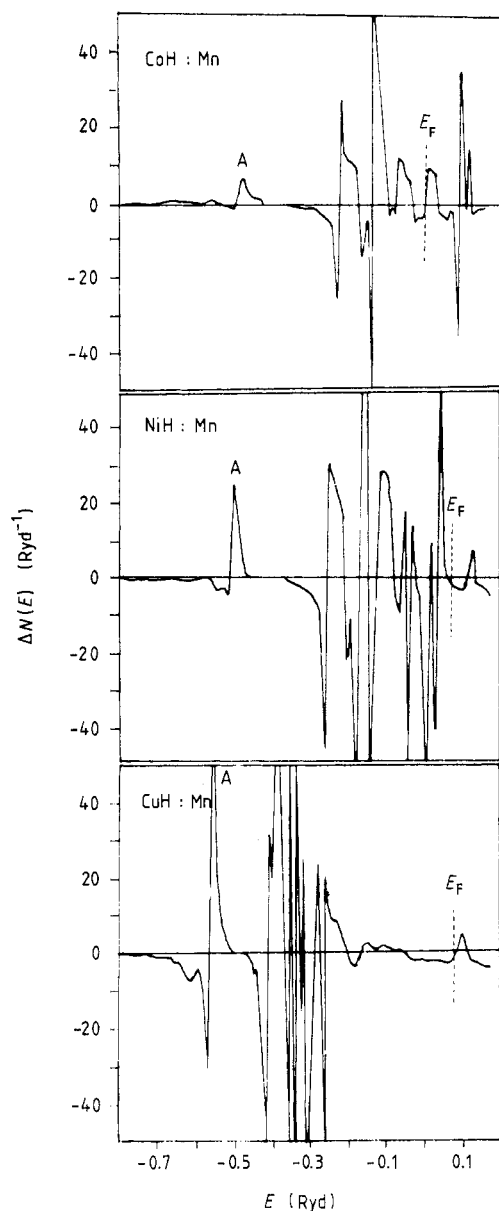


Figure 4. Variations in DOS for CoH, NiH and CuH as an Mn impurity is introduced into these compounds.

shifts from E_F . The quantities $N^{\text{imp}}(E_F)$ decrease sharply, primarily owing to progressive filling and the low-energy shift of d states (table 2), whereas the contributions of the s, p functions to $N^{\text{imp}}(E_F)$ remain small and sufficiently stable.

Consider the impact of impurity effects on the electronic structure of the matrix. To this end, the quantity $\Delta N(E)$, i.e. the variation in the DOS of crystals as an impurity centre is introduced (Ivanovsky *et al* 1988a) was calculated. The results (with reference to the examples of CoH : Mn, NiH : Mn and CuH : Mn systems) are depicted in figure 4.

It is seen that in the region of the upper edge of the H 1s band of the hydrides a well defined positive maximum A arises which coincides in energy with the lowest maximum of the ILDOS, a fact which indicates the formation of Mn–H binding states. In the region of the d band of the hydrides, $\Delta N(E)$ exhibits complicated oscillatory behaviour with

the positive $\Delta N(E)$ maxima corresponding to the TDOS minima and vice versa; this may be treated as the impurity-induced 'smearing' of the structural peculiarities of the DOS of the monohydride and as the formation of a common d-d band in ternary alloys. This tendency can be clearly traced using the data in table 2, which furnishes values of $\Delta N(E)$ for $E = E_F$.

As can be seen, the occurrence of an intensive ILDOS resonance near the Fermi level leads to 'removal' of the matrix states from this region ($\Delta N(E_F) < 0$). Conversely, when $N^{\text{imp}}(E_F) < N^{\text{MH}}(E_F)$, $\Delta N(E_F)$ takes on a positive value, indicating an increase in DOS in this interval for alloyed hydrides.

The quantities ΔE^{imp} for the calculated 3d impurities in CoH, NiH and CuH are presented in figure 2. It is seen that substitution of higher-valence metals for the matrix components turns out to be energetically unfavourable ($\Delta E^{\text{imp}} > 0$); so alloying CoH and NiH with Cu will lead to destabilisation of these compounds. For CuH, the largest gain in binding energy is reached when Co is introduced; this suggests that Co will be the most efficient stabiliser of the cubic structure of CuH.

Many workers (see the review by Oswald *et al* (1985)) note that doping transition metals with atoms of a different species may result in local magnetic moments (LMMS) arising on impurity centres, one of the conditions for local magnetism to form being the presence of an intensive ILDOS resonance near the Fermi level.

As our calculations have shown (figure 3), this situation is typical of d impurities in the middle of the period, when the ILDOS near the Fermi level increase dramatically in comparison with the corresponding values of DOS for ideal monohydrides, thereby leading to instability of the non-magnetic solution of the impurity problem.

Consider the spin-polarisation effects of impurities with reference to the example of PdH. Figures 5 and 6 present results of self-consistent spin-polarised calculations of LDOS for all 3d and 4d metals in β -PdH_{1.0}.

Inspection of these figures shows that shape of the ILDOS, again, has a complicated structure, which indicates considerable hybridisation of impurity-matrix states, and the main tendencies of the ILDOS transformation in the series of the d centres involved are on the whole similar to those described earlier. Allowance for spin-polarisation effects leads, however, to a noticeable energy splitting of spin-up and spin-down impurity states; the states with spins up turn out to be fully occupied, whereas those with spins down lie preferentially above E_F for the alloys and are vacant. As a result, considerable LMMS, arise (figure 7) on the impurity centres (in the middle of the period).

The LMMS of atoms in FCC Pd, obtained by the KKR (Oswald *et al* 1986) and LMTO GF (Antropov 1987) methods are also shown in figure 7. It is seen that the general tendencies of the variation in LMM in the series of 3d metals for Pd tally completely with those for PdH. In other words, the local magnetism of d centres in Pd and its hydride is due primarily to peculiarities in the hybridisation of the external states of d elements and Pd (whereas the role of H is effectively to increase the d-band width), to partial devastation of the outer impurity band (owing to the formation of low-lying H 1s-d-like states) and, as a consequence, to some systematic decrease in the LMM in PdH:M (figure 7).

The magnetic properties of dilute alloys of d metals in PdH have been investigated by a number of workers (see the reviews by Alefeld and Völkl (1978) and Geld *et al* (1985)). It has been established that the introduction of Mn, Fe and Co impurities into the β -hydride leads to giant magnetic moments on these impurities (e.g. about $5.89\mu_B$ for Fe and $5.88\mu_B$ for Mn). Note that, as the content of these additions is increased, the spins align in an ordered fashion.

To calculate giant magnetic moments in β -PdH containing d-metal impurities, a self-consistent description of the polarisation of nearest Pd atoms is required. Such a

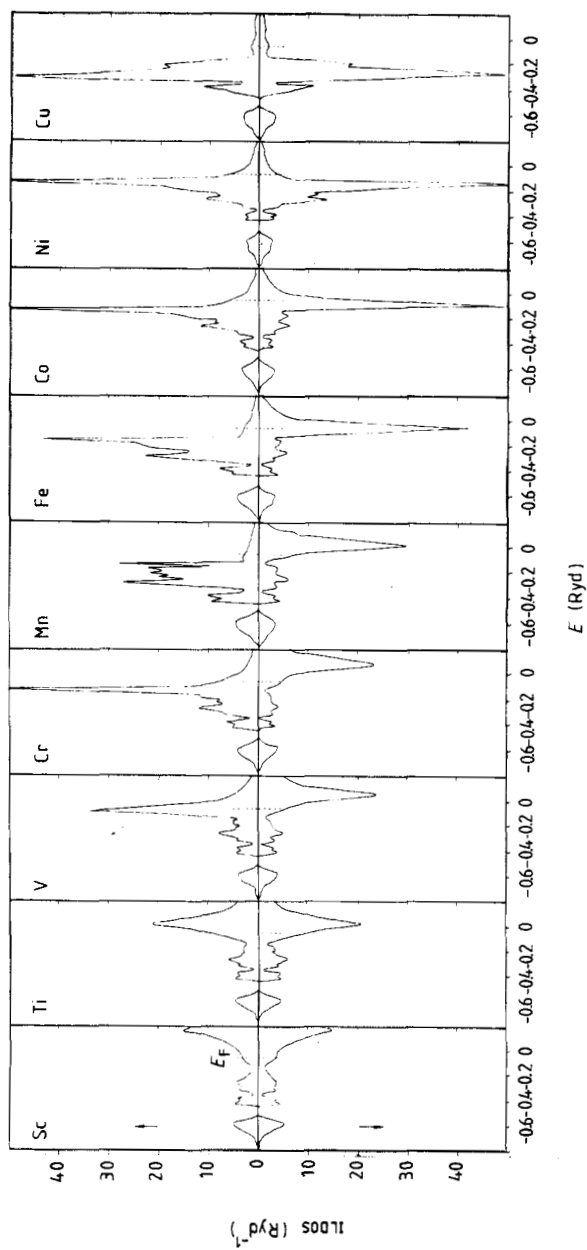


Figure 5. ILDOS of 3d impurities in PdH.

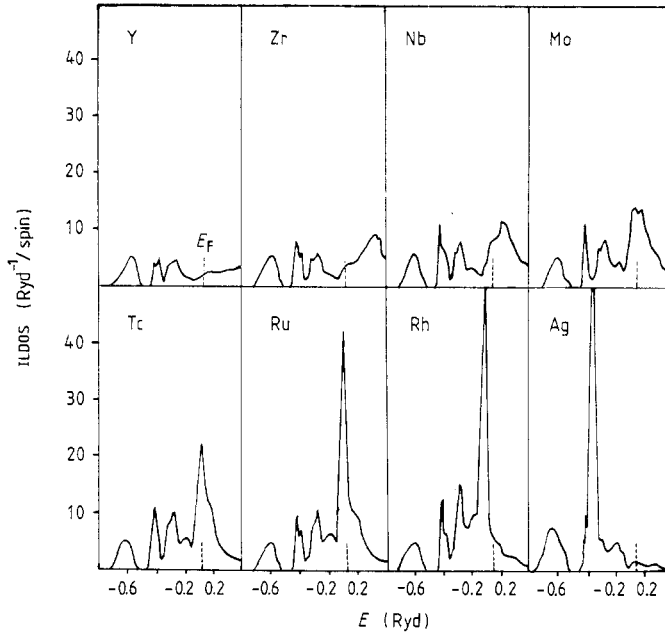


Figure 6. ILDOSS of 4d impurities in PdH.

description is possible, for example, in terms of the implanted-cluster method (Oswald *et al* 1986). However, even the one-impurity problem already suffices to obtain values of total magnetic moments (determined by the Lloyd formula (Anisimov *et al* 1988)) that appreciably exceed the local magnetic moment of the impurity and indicate strong polarisation of the surrounding crystal ($M \approx 0.5\mu_B$).

The situation is different for PdH that contains 4d impurities, as shown in figure 6 and table 3. It is seen that, although the general regularities in the formation of and variation in the ILDOSS of 3d and 4d atoms in PdH coincide (figures 5 and 6), there are no

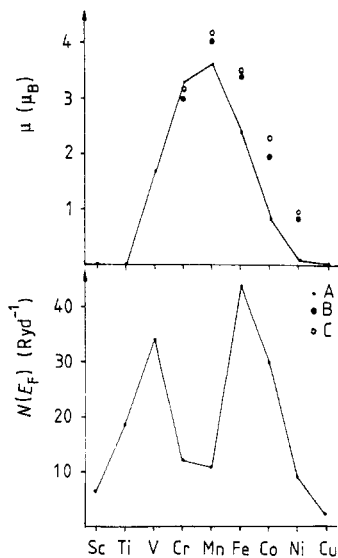


Figure 7. LMMS and DOSS at the Fermi level for 3d impurities in PdH (A), and also in metallic palladium according to calculations (Antropov 1987) (B) and (Oswald *et al* 1986) (C).

Table 3. Some electronic and energetic parameters of 4d-metal impurities in Bi-PdH.

Metal	$N(E_F)$ (Ryd ⁻¹ /spin)			Contributions of individual states to $N(E_F)$ (Ryd ⁻¹ /spin)			ΔE (Ryd)	Contributions of impurity states to spectral sub-bands (electrons/spin)						Centres of d band (Ryd)
	s	p	d	H-like sub-band				M d, s-like sub-band			4d			
				5s	5p	4d		5s	5p	4d				
Y	2.114	0.071	0.512	1.531	0.364	0.153	0.158	0.251	0.086	0.287	0.565	0.369		
Zr	3.977	0.071	0.511	3.395	0.191	0.179	0.172	0.291	0.076	0.271	1.011	0.088		
Nb	8.480	0.074	0.529	7.877	0.154	0.194	0.184	0.311	0.073	0.269	1.469	-0.043		
Mo	14.325	0.075	0.500	13.750	0.111	0.192	0.175	0.299	0.069	0.250	2.015	-0.099		
Tc	15.267	0.075	0.453	14.739	0.070	0.182	0.158	0.278	0.060	0.223	2.593	-0.134		
Ru	13.450	0.074	0.408	12.988	0.050	0.171	0.141	0.253	0.064	0.265	3.106	-0.147		
Rh	6.294	0.075	0.386	5.833	0.027	0.169	0.134	0.268	0.061	0.185	3.683	-0.203		
Ag	1.351	0.094	0.566	0.691	0.053	0.232	0.201	0.692	0.068	0.264	3.543	-0.428		

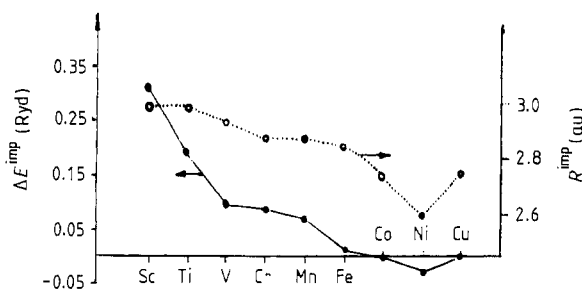


Figure 8. Values of ΔE^{imp} and R^{imp} for 3d impurities in PdH.

LMMS for the above atoms. Apparently, this is primarily because the density of impurity states at the Fermi level and the effective Stoner exchange parameter for 4d atoms decreases dramatically in comparison with that for 3d atoms.

For the example of PdH: 4d metal systems, we illustrate the major mechanisms by which chemical bonding of impurity centres occurs in a hydride (similar data have been obtained also for 3d elements). From table 3, which furnishes decompositions of LDOS into partial contributions to the principal spectral regions of PdH, it follows that, just as for Pd in its hydride, d atoms enter into a hybrid interaction with H 1s states, the d, p, s functions participating in the organisation of these bonds. As the valence of the metal is increased, the contributions of the aforementioned states to the H 1s-like sub-band vary insignificantly. Conversely, the filling and low-energy shift of the impurity d sub-band leads to enhancement of the impurity–matrix d–d interaction.

Quantitative estimates of the alloying effects on the general energetic state of PdH: M alloys were made using the quantities ΔE . The data are presented in figure 8 and table 3. As can be seen, $\Delta E > 0$ for all 3d and 4d atoms except Co and Ni. The quantity ΔE (whose positive value indicates that alloying the matrix and the additions under consideration is energetically unfavourable) grows rapidly with increasing valence of the metal introduced. As follows from these calculations, this fact may be attributed primarily to weakening of M–Pd bonds, whereas Ni and Co will dissolve in PdH exothermally.

Again, just as for the magnetic characteristics of the systems investigated, a behavioural similarity (with respect to the formation of a sss) may be established for Pd–M and PdH–M alloys. Pd is known to form continuous sss only with Fe, Co, Ni, Cu, Rh and Ag, which have electronegativity and atomic radius values close to those of Pd, whereas the other 3d and 4d elements dissolve in Pd only in restricted amounts (Kornilov *et al* 1966). From our calculations, it follows that for PdH: M when the LDOS of M and Pd coincide (uniformity of chemical bond in the crystal and closeness of effective atomic radii—in our calculations the matrix–crystal–atom and impurity–atom radii were varied, with the requirement that the impurity atoms should be electroneutral (Akai *et al* 1984)), the interstitial energy of the first of the above 3d and 4d elements is close to zero or negative, which is a favourable factor for the formation of continuous homogeneous sss of these metals in the hydride.

Conversely, as the deviation of the valence of the impurity from that of Pd increases, their LDOS become dramatically different (especially in the region adjacent to the Fermi level (figures 5 and 6)), and ΔE and the impurity radii increase rapidly (the increase in atomic radii may be responsible for the formation of strong lattice relaxation around an impurity centre), testifying to destabilisation of the system. As a result, compounds with individual structural types will form. A number of such compounds have been described by Jatriš and co-workers.

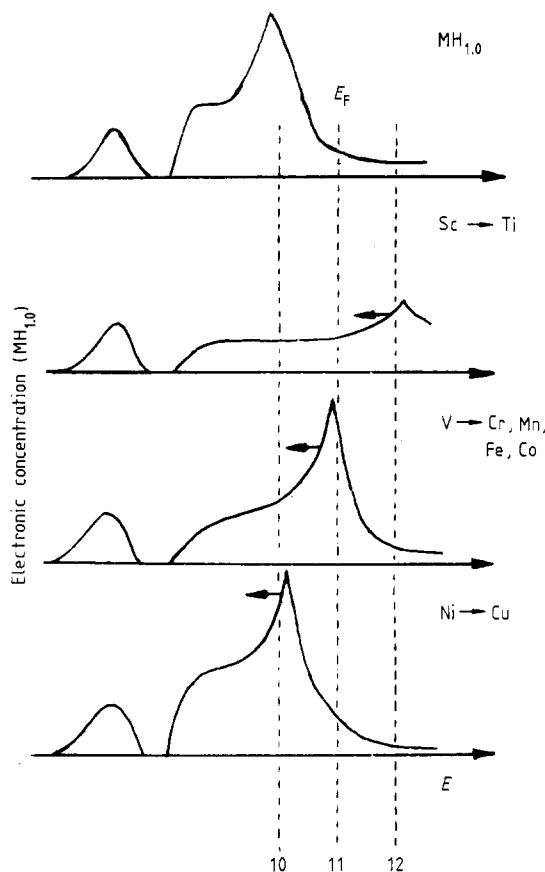


Figure 9. General model of electronic states of substitutional metallic impurities in cubic d-metal monohydrides.

Taken in their entirety, the calculations performed permit us to propose a general scheme of the energy distribution of substitutional metallic impurity states in cubic monohydrides (figure 9). According to this model, the ILDOS of highest-subgroup metals overlap fully with the valence band of the matrix, replicating roughly the TDOS profile of the latter. For subgroup Va–VIIa metals the shape of the ILDOS changes markedly; the contributions of the impurity states to the d band of the hydrides fall appreciably, and an intensive impurity-state resonance arises in the region of the upper edge of the d band; these factors indicate weakening of the total impurity–matrix interaction and are responsible (owing to the spin splitting of the LDOS) for the local magnetism of the alloying centres. Finally, for subgroup IIIa and IVa metals the degree of overlap of filled states of crystals and ILDOS weakens still further; the ILDOS lie for the most part in the conductivity region of the crystal and these additions in hydrides become non-magnetic again.

Assuming the proposed model as a basis permits one to analyse the range of applicability of the rigid-band model. Evidently, the constancy of the DOS of the matrix and of the alloys based on it will take place when monohydrides are alloyed with higher-subgroup metals (Co, Ni, Cu, Rh, Pd, Ag, etc) and the DOS of hydrides and the ILDOS have a common shape. For all the other elements, drastic differences between the ILDOS and the DOS of the matrix do not allow these alloys to be considered in the rigid-band approximation, calling for quantitative calculations for each system of a particular composition.

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