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LOCAL MODES OF INTERSTITIAL ATOMS
IN TRANSITION METALS

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Introduction

Metal-hydrogen systems have been extensively studied by inelastic neutron scattering (INS) for the past two decades [1-13]. The p-elements (oxygen, nitrogen, carbon) have a stronger effect on the mechanical, radiation and other properties of the transition metals, but have been studied much less.

The method of INS is suitable for the study of interatomic interactions in solid solutions. Indeed, the local modes (LM) of hydrogen or p-elements have frequencies above the boundary of the host metal spectrum. In this case, the positions of the LM yield information about the metal-interstitial potentials and site positions. The changes in metal-metal interactions can be derived from the acoustic part of the INS spectrum. The width of the LM give information about interstitial-interstitial interactions in the solid solutions.

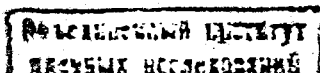
Our group [14-20, 22-28] mainly measured the LM of p-elements with time-of-flight spectrometers: the 'direct' geometry DIN-2PI and 'inverse' geometry KDSOG-M at the IBR-2 reactor, Dubna, and the 'direct' geometry spectrometer at the IR-8 reactor of Kurchatov Institute. The high luminosity of these spectrometers allowed us to measure p-element LM down to 1 at% of the interstitials.

The purpose of this work was to collect the LM data and to analyse their behaviour along transition metal rows of the periodic law.

Influence of interstitials on metal bonds

Alloying transition metals of Group III-V with p-elements as with hydrogen leads to an increase in the metal bond in spite in the increase of the metal-metal distance at interstitial charging. The experimental data for hydrogen-metal systems were reviewed in [29]. The data for these metals with p-elements are in [14-24].

The main reason of enhancement of the metal bonds in these metals is reconstruction of the electron bands. Interstitials add the electrons to the valence bands, shifting the Fermi level to a lower concentration. This decreases the ion-ion screening effects and increases the metal bond [14,29].



At the ends of the rows, the antibonding levels of the interstitials coincide with the Fermi level and make the metal bond weaker [30] (for example, H in Pd [29], C in iron martensite [19]).

Metal-interstitial interactions

The LM energies in transition metal solid solutions were gathered in Tab.1 for hydrogen and in Tab.2 for p-elements. The experimental LM data were used for calculating of the Me-X (X=H,O,N,C) force constants γ_X . The γ_X values (Tables 1,2; column 5) were calculated for central forces between nearest Me-X atoms using the frozen lattice approach [31]. The accuracy of this calculation is 15%, but it is not important for further discussions. The force constants were showed in Fig.1 as functions of Me-X distances. For comparison, the same dependence for MeH₂ hydrides (Ross's curve [12]) is showed as "H in hydrides".

It should be noted that the Me-X distance r_{Me-X} , calculated from the lattice parameters of solid solutions (Tab.1,2; column 4) does not account for local distortions near the interstitial atoms. These distortions are approximately 0.05 Å for the closed packing of FCC and HCP lattices [16] and up to 0.5 Å for the BCC lattice [31]. If we take these relaxed distances into account, we cannot construct the smooth empirical dependencies for $\gamma_X(r_{Me-X})$.

A second note is that in Tab.2 we include the INS data for α -TiO_{0.5}, NbO, β -V₂N, TiN, ZrN for Me-O and Me-N which coincide with the curves for solid solutions. But, the optical modes of the MeC monocarbide's departure greatly from the LM solid solution data and can not be represented by a single smooth curve. The possible reason for this will be discussed later.

The Figure 1 shows the following force constant characteristics of interstitials in transition metals:

1. The Me-p-element force constants are 2-4 times greater than the Me-H constants.

2. The Me-H force constants for H in the tetrahedral positions (TP) of solid solutions and of hydrides are close.

3. The Me-H force constants for H in octahedral positions (OP) of solid solutions are half as large as for H in TP (Fig.1)

4. All curves in Fig.1 can be fitted by polynomials of third degree so that they transform into straight lines from the r_{Me-X}^{-3} argument (Fig.2). The curve for H in OP, as an exception, follows the exponential law:

$$\gamma_H = 0.819 + 6.18 \cdot \exp[-(r_{Me-H} - 1.57)/0.158]. \quad (1)$$

Discussion

The reason for sharp increase in $\gamma_X(r_{Me-X})$ for OP interstitials at $r_{Me-X} \geq 1.8$ Å (Fig.1) is the enhancement of the Me-X repulsion due to an increase in the structure incommensurate with the interstitial atom size and the interatomic space of the host. At $r_{Me-X} > 2.1$ Å (Fig.1), the interstitials more or less freely enter the metal lattice and a further increase in r_{Me-X} leads to a decrease in the Me-X bond and force constants.

The behaviour of p-interstitials in transition metals does not fully described by quantum-mechanical theory. At present, only the effective-medium theory (EMT) is available [33,34]. This theory calculates the embedding energies $\Delta E^{emb}(n)$ for an atom as function of the electron gas density n . Figure 3, reproduced from [33], shows $\Delta E^{emb}(n)$ for the studied atoms and He. We can compare Fig.2 and Fig.3. Indeed, the r_{Me-X}^{-3} parameter is proportional to the electron density in the interstitial spaces. Following by [34], we can roughly estimate the density n for OP in transition metals as

$$n = 1.9/V_{W-Z}, \quad (2)$$

where V_{W-Z} is the volume of the Wigner-Seitz site. These n values are displayed in the upper scale of Fig.2.

The comparison of Fig.2 and Fig.3 reveals the dependence of $\gamma_X(r_{Me-X})$ on $\Delta E^{emb}(n)$. The $\Delta E^{emb}(n)$ has minimums at $n \approx 0.005$. In this region, the $\gamma_X(r_{Me-X})$ is determined by the Me-X bonds, as discussed earlier. The increase in n results in an

increase in of $\Delta E^{\text{emb}}(n)$ due to the growth in the repulsion of an atom from the electron gas [33]. This increase in repulsion also increases the force constants (Fig.2). The derivatives of both $\gamma(r_{\text{Me-X}}^{-3})$ and $\Delta E^{\text{emb}}(n)$ increase with atomic number (Tab.3). Table 3 shows these derivatives with Z_{eff} , the effective number of electrons sensitive to the environment [33]. For hydrogen, we include data for TP hydrogen in solid solutions.

The values of $\Delta E^{\text{emb}}(n)$ at the minimums (Fig.3) contradict both the experimental data for the chemical bonds in carbides, nitrides, and oxides [33] and the quantum-mechanical calculations for these compounds with Ti and Ni [35]. The chemical bonds and p-X - d-Me hybridization decrease in the C-N-O row. The minimums of $\Delta E^{\text{emb}}(n)$ should follow this row. The discrepancy can be explained by the restriction of EMT to the correct account of p-X - d-Me hybridization. This correction is needed, as was shown for Me-H systems in [34].

The essential p-X - d-Me hybridization in Me-C systems can explain the departure of the carbide optical modes from the $\gamma_X(r_{\text{Me-X}})$ for carbon LM in solid solution. The increase in carbon concentration drastically changes the valence electron band and chemical bond contrary to the Me-N and Me-O systems, where a p-like resonance forms at bottom of the d-band [35].

The substantial role of the Me-X repulsion in the studied systems allows the EMT to be applied to these systems. A correct accounting for covalent bonds, lattice relaxation and actual electron density in transition metal sites is needed.

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Table 1
Local modes of hydrogen in transition metal solid solutions

Position	Me-H	$h\omega$, meV	$r_{\text{Me-H}}$, Å	γ_{H} , 10^4 dyn/cm	Reference
OP	α -TiOH _{0.03}	90±2	2.08	1.55	[1]
	α -PdH _{0.02}	68.5±2	1.95	0.90	[2]
	β -V ₂ H	221±5	1.515	9.35	[3]
		63±2	2.12	0.76	
	α -MnH _{0.07}	74±2	2.24	1.05	[4]
		108±2	1.9	2.23	
		123±2		2.90	
	β -NiH _{0.1}	90±2	1.86	1.55	[5]
	α -CoH _{0.056}	120±2	1.78	2.76	[6]
CeH ₃	62±2	2.75	0.74	[7]	
LaH ₃	60±2	2.77	0.69	[7]	
TP	α -CeH _{0.04}	96.2±1	2.234	2.66	[8]
	α -ScH _{0.35}	103.5;147.5	1.98	4.49	[9]
	α -YH _{0.07}	100; 135	2.15	4.14	[9]
	α -ThH _{0.05}	114±5	2.20	3.74	[10]
	α -TiH _{0.05}	141±1	1.755	5.63	[11,12]
	α -ZrH _{0.05}	144±1	1.93	5.96	[11,12]
	α -VH _{0.012}	106;170	1.692	4.79	[13]
	α -NbH _{0.0056}	106;163	1.845	4.20	[13]
α -TaH _{0.037}	114;154	1.84	4.22	[13]	

OP (TP) - H in octahedral (tetrahedral) position, $h\omega$ - energies of the hydrogen LM, $r_{\text{Me-H}}$ - unrelaxed Me-H distances, γ_{H} - Me-H force constants.

Table 2
Local modes of O,C,N-p-elements in transition metal solid solutions

X	Me-X	$h\omega$, meV	r_{Me-X} , Å	γ_X , 10^4 dyn/cm	Reference
O	α -VO _{0.03}	91±2	1.515	23.62	[14]
		55.1±1	2.143	8.65	
	α -VO _{0.06}	86±2	1.530	21.19	[14]
		56.7±1	2.164	9.17	
	α' -VO _{0.11}	84±2	1.555	20.12	[15]
		57.9±1	2.157	9.56	
	β' -VO _{0.2}	79±5	1.66	17.8	[15]
		58±2	2.114	9.73	
	α -TiO _{0.04}	60.5±1	2.081	9.83	[16]
	α -TiO _{0.5}	54.4±1	2.135	7.91	[16]
α -ZrO _{0.05}	52.7±1	2.268	7.92	[16]	
α -ZrO _{0.41}	52.3±1	2.278	7.81	[16]	
α -NbO _{0.03}	50.0	2.337	7.13	[17]	
α -YO _{0.03}	40; 50	2.541	5.77	[18]	
C	α -FeC _{0.05}	96±4	1.43	19.71	[19]
		68±2	2.022	9.89	
	γ -FeMnC _{0.04}	76±2	1.810	12.35	[20]
ThC _{0.06}	43.8±0.5	2.542	4.10	[21]	
N	α -VN _{0.02}	97±2	1.52	23.48	[14]
		70±1	2.14	12.23	
	β -V ₂ N	80±1	1.99	15.10	[22]
	VN	70±1	2.07	12.23	[23]
	α -Ta ₂ N _{0.02}	92.5±2	1.62	21.35	[24]
		60.5±1	2.342	9.133	
	β -Ta ₂ N	73±1	2.146	13.3	[25]
	α -TiN _{0.05}	73±1	2.09	13.3	[26]
	α -TiN _{0.2}	71±2	2.097	12.58	[27]
	TiN	68±2	2.15	11.54	[27]
	ZrN _{0.3}	62±2	2.28	9.59	[27]
	γ -FeMnN _{0.02}	78±1	1.80	15.18	[28]
	γ -FeMnN _{0.04}	74±1	1.82	13.66	[28]
Mn ₄ N	72±2	1.94	12.94	[26]	

$h\omega$ - energies of the p-elements LM, r_{Me-X} - unrelaxed Me-X distances, γ_X - Me-X force constants.

Table 3
Correlations of the effective charge Z_{eff} , and embedded energy derivatives dE/dn [33] with force constant derivatives $d\gamma_X/dr^3$ for the studied interstitials.

	H	C	N	O
Z_{eff}	0.731	2.97	3.15	3.61
dE/dn , eV/a.u.	136	545	590	682
$d\gamma_X/dr^3$, eV/Å ⁴ ×10 ⁻⁵	290	327	424	453

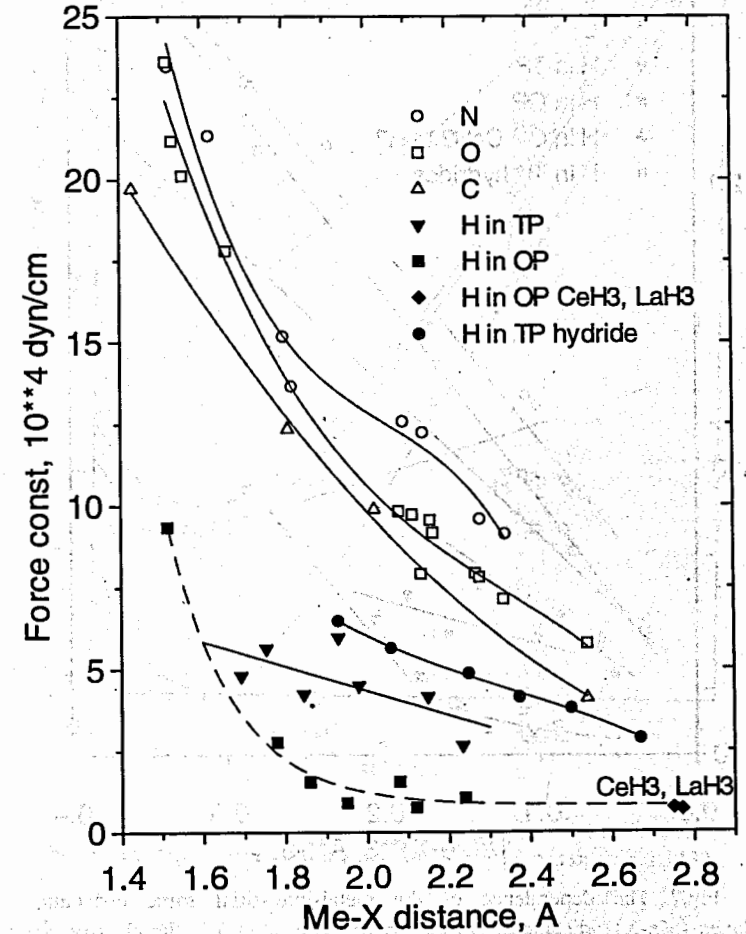


Fig.1 The dependence of the metal-interstitial force constants versus unrelaxed metal-interstitial distances. "H in hydride" indicates the Ross curve [12], the points "CeH₃" and "LaH₃" are for octahedral hydrogen in these hydrides.

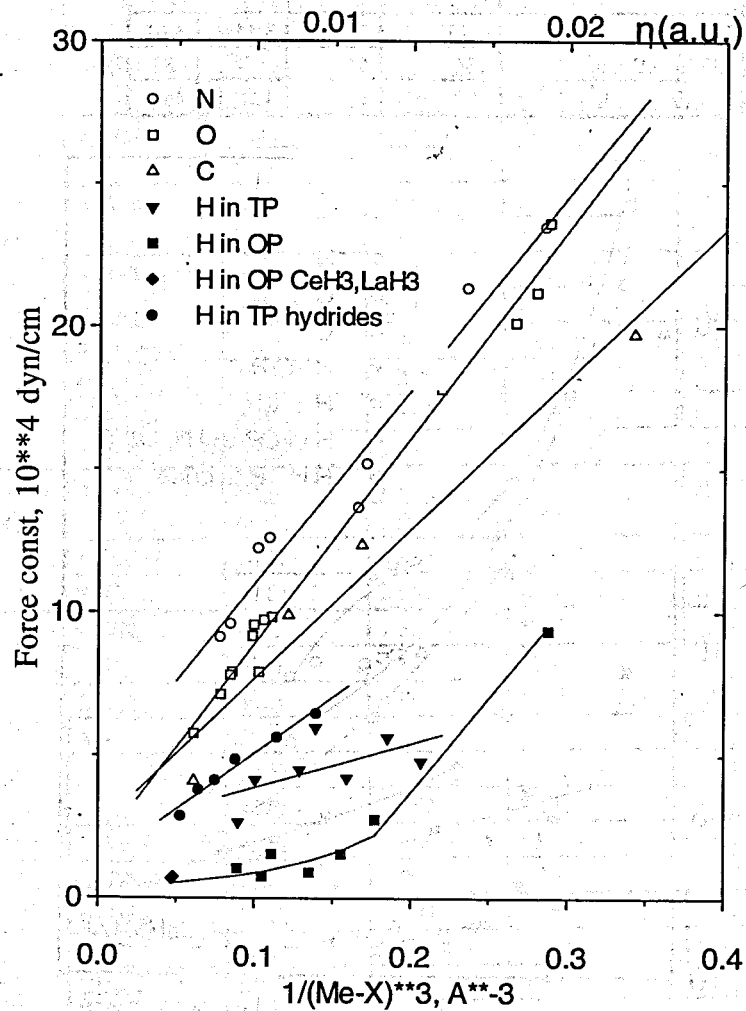


Fig.2 The dependence of the metal-interstitial force constants versus unrelaxed $(Me-X)^{-3}$ distances. On the upper scale: $n(a.u.)$ is the electron density in atomic units.

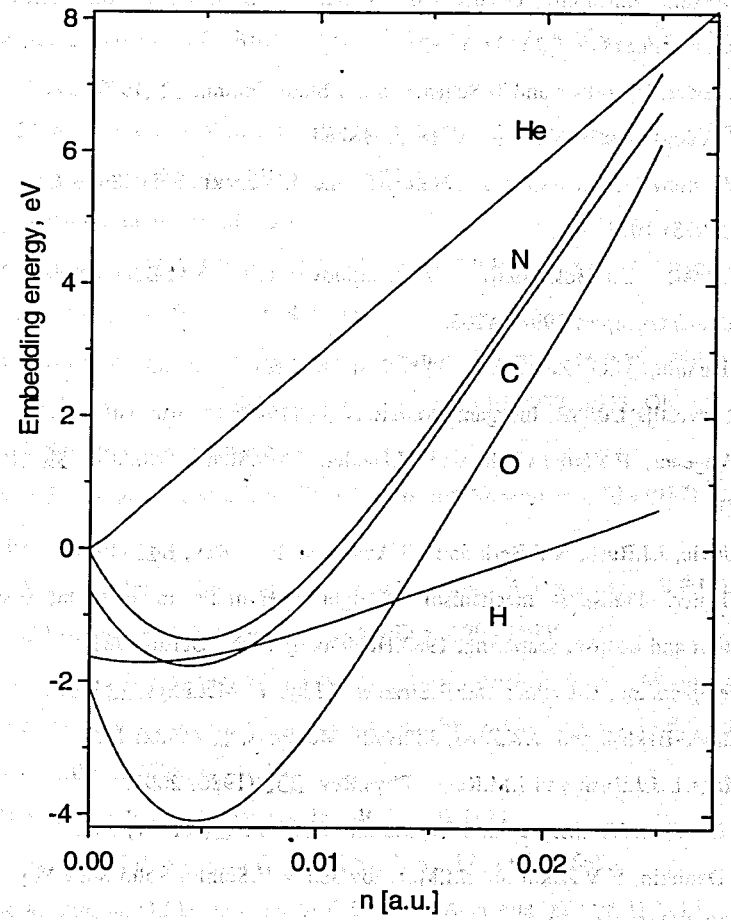


Fig.3 The dependence of the embedded energies versus $n(a.u.)$ [33].

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