Hydrogen interaction with dissolved atoms in metal solid solutions

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Abstract

The H(D) atom's interaction with one another, other "heavy" interstitial atoms (O, N, and C), and substitutional atoms is analyzed on the basis of strain-induced (elastic) interaction. The interaction energies are calculated for bcc, fcc, and hcp metal solid solutions with regard to the discrete atomic structure of the host lattice. In all cases, the coordination shells of both types – with attraction and with repulsion – exist. The interaction energy dependence on the distance is due mainly to the crystal lattice type. The H–H strain-induced interaction energies are compared with the available literature data from first principle calculations. The strain-induced interaction should be supplemented by repulsion in the nearest coordination shells for the case of interstitial–interstitial interaction and by chemical interaction in the case of H-substitutional interaction. The examples are given for the use of the strain-induced interaction energies in calculations of the long-range order and relaxation processes.
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1. Introduction

The interaction of the dissolved atoms affects the atom arrangement and energies and thereby influences the structure and properties of solid solutions. By 'atom arrangement', we mean the creation of short-range or long-range order and different atomic complexes, which are a sort of short-range order. Change in the energies of dissolved H atoms in a solid solution due to the atoms' interaction influences diffusion, relaxation and other processes.

The determination of energies of hydrogen interaction with other dissolved atoms is an actual problem. A number of methods for this determination are based on the use of experimental data by neutron diffraction, NMR, internal friction and so on. However, reliable estimations carried out on the basis of model analysis of the corresponding data are difficult even taking into account only the nearest-neighbor interactions.

There are many methods for calculating interaction energies, but in the case of interstitial atoms the methods based on 'the first principals' have very limited usage only and they do not provide the total picture of H–H(D–D), H(D)-substitutionals and H(D)–O(N,C) interactions in the metals with different types of crystal lattice. The indirect elastic interaction calculated in the framework of a discrete crystal lattice (the so-called "strain-induced interaction") plays a significant role [1–3]. Such interaction was calculated for many solid solutions and it was used successfully for analysis of structure and properties. In this paper, we will describe the strain-induced interaction model and some examples of its application to the analysis of the relation between the dissolved atom interaction and structure and property peculiarities in interstitial and interstitial–substitutional solid solutions in metals.

2. Strain-induced interaction of dissolved atoms

Strain-induced interaction is the indirect interaction of dissolved atoms in a discrete crystal lattice due to displacements of host atoms under the forces originating from dissolved atoms. This interaction is elastic in its nature. The method

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for calculation of the strain-induced interaction energy for a monatomic Brave lattice is described in Khachaturyan's books [1,2], and the method used for a polyatomic lattice appeared in the book of Bugaev and Tatarenko [3].

In such calculations based on the lattice static equation, the coefficients of the concentration expansion of the host lattice u_{ij} are used to describe the elastic distortions created by dissolved atoms in a crystal lattice of the metal–solvent. These coefficients are calculated using the lattice period values determined by the X-ray diffractometry methods. To describe the elastic reaction of the metal crystal lattice, the elastic constants of the metal–solvent and its phonon spectrum in the form of Born-von-Karman constants are used. In this way, relevant experimental information is used in these semi-phenomenological calculations, thus greatly increasing the reliability of the results. The solid solution type (interstitials located in the octahedral interstices; interstitials located in tetrahedral interstices; substitutional atoms located in lattice points) and the crystal lattice type are taken into account. A detailed description of the calculation method can be found for both bcc and fcc solid solutions in [1,4,5] and for hcp solid solutions in [3,6–8].

2.1. Characteristics of strain-induced interaction

Examples of the energies of the H–H, H–O(N) and H–s strain-induced interaction are shown in Figs. 1–3 (here, the negative energy represents attraction, and the positive energy represents repulsion). The following features can be observed: (a) The interaction is oscillating. This means that the energy does not decrease steadily as the distance separating interacting atoms increases. (b) The interaction may be anisotropic. This means that there exist the coordination shells with the same distance between the interacting atoms but with different mutual arrangements and therefore with different values of interaction energy. (c) The interaction is of long-range nature. In the sufficiently removed spheres, significant repulsion and attraction exist that can contribute significantly, especially to the configuration energy of the solid solution. It is obvious that it is impossible to restrict the interaction taken into account by one or two coordination shells only, as it was reported in many papers where the interaction energies were evaluated based on any experimental data.

The energies can vary anywhere from 0 eV (H–Ta in Nb or H–Nb in Ta) to −0.94 eV (H–N in Nb, the first coordination shell [9,12]) depending on the type of solute atoms (interstitials in octahedral or tetrahedral interstices; substitutials in the lattice points); the crystal lattice type; the elastic properties of the host metal (Born-von-Karman constants); and the distortions caused by dissolved atoms in a solid solution (the concentration expansion coefficients of the host lattice u_{ij}). It is impossible to point out in each case why the interaction is stronger or weaker, but some features can be pointed out: (1) in all cases, the coordination shells with attraction are present; (2) in the bcc and fcc solid solutions, the H in-
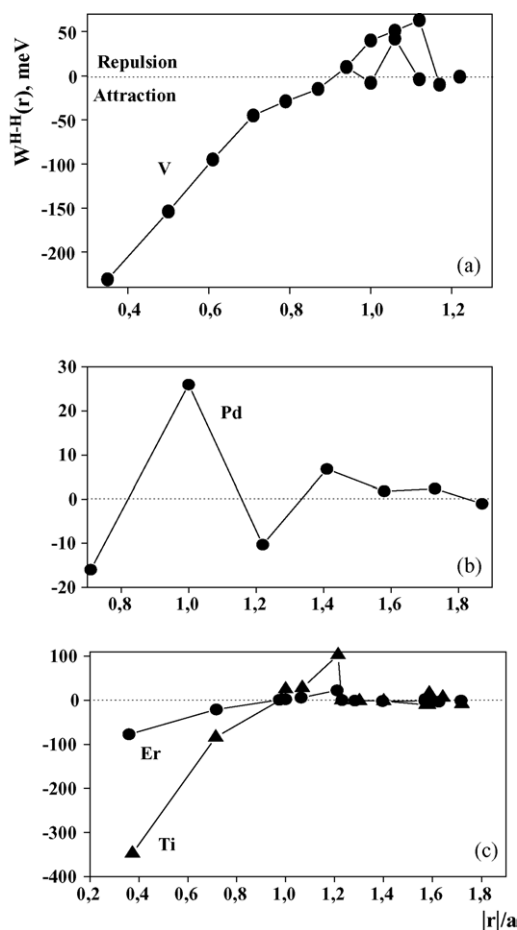

Fig. 1. The interaction energy for two hydrogen atoms as a function of the distance between them in bcc (a) [9], fcc (b) [16] and hcp metals (c, Er [8] and Ti [20]).
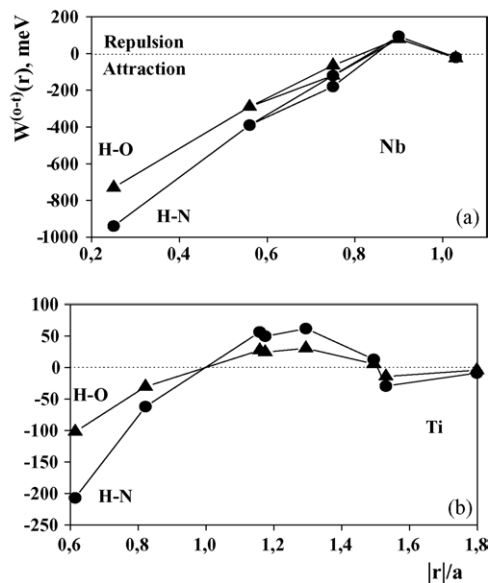

Fig. 2. The interaction energy of a hydrogen atom with a "heavy" interstitial atom as a function of the distance between them in bcc (a) [11,12] and hcp metals (b) [20].
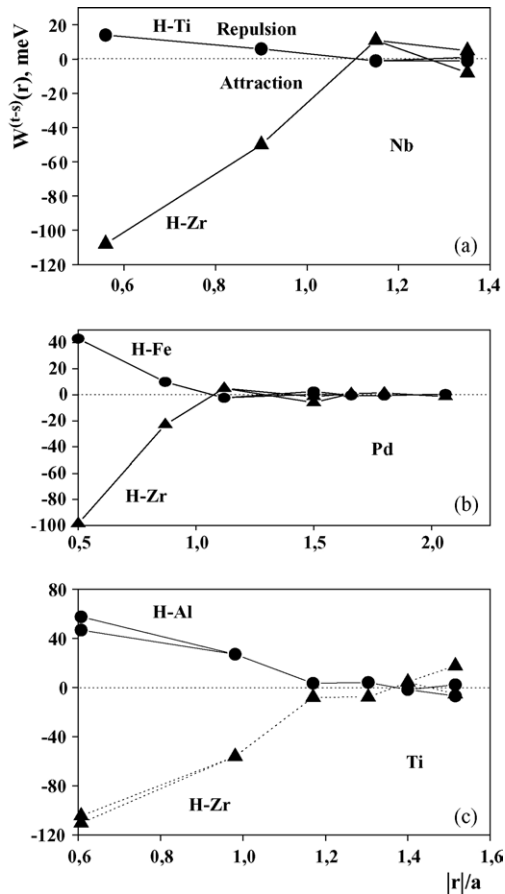
Fig. 3. The interaction energy of a hydrogen atom with a substitutional atom as a function of the distance between them in bcc (a) [14,39], fcc (b) [18] and hcp metals (c) [20].

Table 1
The alloys for which the strain-induced interactions of hydrogen with dissolved atoms are calculated

Crystal lattice	Host metals	Type of interaction	References
Bcc	Ta	H–H, D–D	[10]
	V, Nb, Ta	H–H	[4]
	V, Nb, Ta	O–H, N–H	[11]
	V, Nb, Ta	O–H, N–H	[12]
	α-Fe	H–s, H–C, H–N	[13]
	V, Nb, Ta	H–s	[14]
	Nb	H–H	[15]
	V, Cr, Mo, W, α-Fe	H–H	[9]
Fcc	Pd	H–H	[16]
	Ni, Al, Cu, Au, Ag	H–H	[9]
	γ−Fe	H–H	[17]
	Al, Cu, Ni, Ag, Au, Pd, Pt	H–s	[18]
	Ni	H–H	[19]
Hcp	α-Ti, Tc	H–H	[6]
	α-Ti, Y	H–H	[7]
	Sc, Y, Tb, Dy, Ho, Er, Lu	H–H, D–D	[8]
	α-Ti, α-Zr, α-Hf	H–H, D–D, H(D)–O(N,C)	[20]

teraction with the light interstitial atoms (H and D) is much weaker than that with heavy interstitial atoms (C, O, and N) due to smaller values of u_{ij}. In the hcp Ti, Zr and Hf, the reverse relation is observed because the O, N, and C atoms dissolved in the octahedral interstices distort the crystal lattice less strong than the H, D atoms in tetrahedral interstices. (3) The dependence on distance is mainly determined by the crystal lattice type. However, in one type of crystal lattice, it is determined by the interstice type. (4) The sign of the H–s interaction energy in a given coordination shell is determined for the different substitutional atoms by the sign of the concentration expansion coefficients of the substitutional atoms (these atoms either compress or expand the crystal lattice).

The alloys for which the strain-induced interaction energies are published in the literature are listed in Table 1.

2.2. Applicability limitations of the strain-induced interaction model

It is well known that elastic interaction is not the only type of interaction. As it can be seen from Figs. 1 and 2, the H(D) atoms are attracted to one another or to the heavy interstitial atoms in the nearest coordination shells in the framework of this model. At the same time, analysis of the structure of hydrides [21] showed that it was necessary to supplement the long-range elastic interaction in bcc metals with a short-range repulsion of interstitials (so-called 'hard core'). Calculations of the electron contribution in the H–H interaction energy are carried out for a limited number of metals (Pd [16], Nb [15], Y [22], and Zr [23]) and for a limited number of coordination shells only, thus making difficult their comparison with the energies calculated on the strain-induced interaction model. All these calculations show that the H–H interaction is repulsive in the closest interstitial sites. This fact corresponds to the Switendick criterion [24] that determines the H–H repulsion distance ('hard core') in the metals as equal to 0.21 nm.

By this means using the H–H interaction energies the elastic interaction energies should be supplemented by additional repulsion in the nearest coordination shells. Two possible ways for introducing this repulsion are described in the literature: (a) using the H–H direct interaction energies from the data for the hydrogen molecules [6,7,19] assuming that the crystal lattice of the metal does not affect the electron interaction of the dissolved hydrogen atoms. The energies of this "electrochemical interaction" are summarized with the strain-induced interaction energies in each coordination shell. This is a very rough approach; (b) blocking the interaction in several nearest coordination shells [1,9,12,25]. The repulsion distance was determined through Monte Carlo simulation of the long-range tracer diffusion coefficients of interstitial atoms or internal friction peaks caused by their "diffusion under stress" and by comparison with experimental data. It was shown that the H–H repulsion for V, Nb and Ta [9] and H–N repulsion for Nb and Ta [9,26] extend up to three coordination shells. Behavior of the hydrogen atoms in

Table 2
Comparison of calculated and experimental temperatures of internal friction peaks [12]

Alloys	Nb–H–O	Nb–H–O	Nb–D–O	Ta–H–O	Nb–H–N	Ta–H–N	Ta–D–O
f (Hz)	0.76	1000	10000	1000	0.76	0.61	20000
$T_{max}^{(cal)}$ (K)	56	74	98	87	65	63	143
$T_{max}^{(exp)}$ (K)	50 [28]	79 [29,30]	106 [30,31]	77 [29]	60 [32]	50 [33]	126 [34]

a solid solution is determined both by a repulsion distance and elastic interaction energies outside the radius of repulsion.

Computer simulation of the temperature dependence of hydrogen diffusion in Pd, Cu, and Ni with a low hydrogen concentration of 0.11 at.% [9] showed that such additional repulsion is absent. This fact is due to the large distance between the hydrogen atoms located in the octahedral interstices in a fcc lattice. In the metals with hcp crystal lattice, only the first coordination shell should be also blocked [27] based on the Switendick criterion [24].

Examples of application of the H(D) interaction energies with other dissolved atoms for analysis of the structure and properties of the alloys are given below.

3. Hydrogen internal friction peak in Nb and Ta [12]

The energies of strain-induced interaction of interstitial atoms were used for the calculation of the peak temperature, T_{max}, of hydrogen-induced internal friction. It is known that the hydrogen Snoek-type maximum is caused by the diffusion under stress of H or D atoms near the immobile O or N atoms [28–34]. Therefore for such calculations one needs the values for the H–H(D–D) and H(D)–O(N) interaction energies.

It was assumed that contributions to the internal friction are created by H and D atoms in the first four coordination shells around the O and N atoms (the distance of the strongest attractive interaction). The H and D diffusion data for dilute H(D)–metal solid solutions were also used. One can see in Table 2, that for many systems the calculated temperature of the internal friction peak is in good agreement with experimental data. This means that the interatomic interaction model is applicable to these solid solutions.

4. Deuterium ordering in Lu–D [27]

An ordered state exists at low temperatures in solid solutions of hydrogen and deuterium in rare earth metals [35,36]. It has been shown by neutron diffuse scattering studies of solid solutions that the H–H or D–D pairs exist in the ordered phases. These pairs are located along the hexagonal *c*-axis in the tetrahedral interstices closest to the metal atom in the sixth shell of tetrahedral interstices around the given tetrahedral interstice, Fig. 4.

A model for the structure of such ordered solid solutions suggested in [37] explains well the neutron diffuse scattering observed. According to the model, the atom pairs form the chains along the *c*-axis (Fig. 4) that occupy two vertical axes located at the distance of $a/\sqrt{3}$ from each other. Such a chain has a length of (3–5) *c* with *a* and *c* being the lattice spacings. The chains are combined into pairs located at the distance of $a\sqrt{3}$ from each other in the basal plane. In [37], two versions of the chain pairs are proposed: in-phase (chains 1 and 2 in Fig. 4) and in-antiphase (chains 2 and 3 in Fig. 4). It is impossible to conclude which version of the pair chains is true by using the diffuse scattering data.

Analysis of the structure of chains consisting of interstitial atom pairs and of the ordered arrangement of such chains requires taking into account the long-range interactions. Thus, it was of significant interest to analyze this ordering by considering the specific energies of strain-induced interactions in many coordination shells, taking into account the "electronic" interaction analyzed in [22]. Such consideration was carried out for the solid solution $LuD_{0.19}$, for which the detailed experimental data are available [37,38].

The configuration part of the internal energy E per interstitial atom was determined by Monte Carlo computer simulation. The modeling proved that it is impossible to explain the existence of ordering with formation of such chains by using the strain-induced interaction model approximation only. Additional attraction in the sixth coordination shell should exist, as it is predicted by calculations [22] of the electronic contribution. But the aligning of these pairs in chains can be explained by the weaker strain-induced (elastic) attraction in the eighth shell. This attraction integrates the D–D pairs of the sixth shell into a chain.
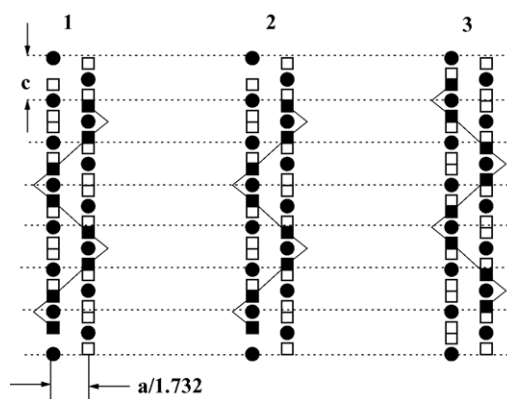

Fig. 4. Chains of deuterium atom pairs along the hexagonal *c*-axis in lutetium (according to [37]). Circles: metal atoms; solid squares: D atoms in tetrahedral interstices; open squares: empty tetrahedral interstices. 1, 2 and 3: individual chains; 1 and 2: a pair of chains in-phase; 2 and 3: a pair of chains in-antiphase.

The interaction energy of two chains $\Delta E_{\mathrm{ch}}(r)$ was calculated by summation of the D–D pair interaction energies in the isolated chains and in the pairs of chains located at different distances and turned in different way relative to each other. As it can be seen from Fig. 4, the $\Delta E_{\mathrm{ch}}(r)$ depends on the interaction energy neither in the 1st shell nor in the sixth. For this reason, the interaction of two chains is determined exclusively by the long-range strain-induced interaction. The interaction energy calculation based on the pure D–D strain-induced interaction model has shown that the in-antiphase chain pairs exist and the chains should be located at the distance $r = a\sqrt{3}$ from each other, the value confirmed by the experiment [37]. This fact proves that the chain pair formation can be explained by the pure elastic interaction of the interstitial atoms that make up the chains.

5. Conclusions

Main characteristics of the strain-induced (elastic) interaction of the H and D atoms with each other and with other types of dissolved atoms are discussed. All solid solutions where such interaction energy was calculated, are reviewed. Based on two examples, hydrogen relaxation in Nb and Ta, and ordering in the Lu–D alloys, the role of such interactions in formation of structure and properties of the metal–hydrogen system is shown.

Acknowledgements

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