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Interatomic potentials and atomistic calculations of some metal hydride systems

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Abstract

The effective interatomic pair potentials for Ti, Zr, Hf, V, Nb, Ta and their hydrides are obtained by inverting the ab initio cohesive energy curves based on the lattice inversion method, and then the inverted pair potentials are used to calculate the mechanical and thermal properties of these hydrides. © 2002 Published by Elsevier Science B.V.

Keywords: Ab initio interatomic potential calculations; Inverted pair potentials; Metal hydrides

1. Introduction

Metal hydrides have attracted a lot of attentions in both fundamental and applied researches due to their important industrial applications. However, some important mechanical and thermodynamic properties of these systems have yet to be studied and understood [1–3]. For example, the understanding of the process of delayed hydride cracking-(DHC) in transition metals remains incomplete because some mechanical and thermal properties are not yet available [4–9]. Hydrogen induced-change of mechanical properties of intermetallics is still an unresolved technical problem in their industrial applications as structural materials [10].

The atomistic simulation is a well-known powerful tool for the studies of structures and properties of materials, of which the interatomic potentials are key ingredients. The use of pair potentials is a physically appealing approach to describe the interatomic interactions in condensed matter. For example, various generalizations of the Morse-type potentials are used for metals [11], and the combination of Born–Mayer potential and Coulomb potential are used for ceramics [12]. The most popular spherically symmetric pair potential, the Lennard–Jones potential that describes the interatomic interactions in Van der Waals solids, is extensively used in the atomistic simulation of many kinds of materials. However, because of fundamental shortcomings of pair potential models [23], many-body potential models have been proposed and developed in recent years. For example, the embedded atom model (EAM) [13–19], Finnis–Sinclair model [20–22] and glue model [23], which can be unified into the theoretical framework of density-functional theory, are used extensively in the transition metals and their alloys. The empirical Stillinger–Weber potential model [24] and Tersoff model [25] have successfully been used for the atomistic simulation of semiconductors. The bond order potential (BOP) [27] and the environment-dependent interatomic potential (EDIP) [26], developed recently based on the original Tersoff model and Stillinger–Weber potential, are the more explicit form of many-body potentials for covalent bond materials. Empirical many-body potential models include adjustable parameters which should be determined by fitting to the experimental data of the involved systems. Since reliable experimental data on mechanical properties of metal hydrides are generally not available (for example the elastic constants), application of these empirical many-body potential models in metal hydrides is limited. To the best of our knowledge, reliable many-body model potentials for metal hydrides are not yet available.

In this paper, we adopt an effective approach, the lattice inversion method [28–31], to obtain the effective pair potentials for Ti, Zr, Hf, V, Nb, Ta and their hydrides from the first-principle band structure total energy calculations. By using the ab initio inverted pair potentials, we calculated the elastic constants, bulk modulus, and thermal expansion property of these systems. In the following Section, we briefly describe of the ab initio total energy calculations and the inversion of pair potentials of the

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involved systems. The atomistic calculations of mechanical and thermal properties of these hydrides are performed and discussed in Section 3.

2. Ab initio total energy calculations and pair potential inversions

The idea of inversion of central pair potentials from cohesive energy curves was first proposed by Carlsson et al. [28]. Lately, the concise formula of lattice inversion method (LIM) was developed by Chen et al., based on the analogy of the obscure Möbius inversion transform in number theory [29–31]. The lattice inversion method can be expressed as the relations between two functions, $F(r)$ and $f(r)$, namely, if

$$F(r)=\frac{1}{2}\sum_{n=1}^{\infty} w(n)f[q(n)r] \tag{1}$$

then

$$f(r)=2\sum_{n=1}^{\infty} \mu(n)F[q(n)r], \tag{2}$$

and

$$\sum_{m\mid\frac{q(n)}{q(m)}} \mu(m)w\left[q^{-1}\left(\frac{q(n)}{q(m)}\right)\right]=\delta_{n1}, \tag{3}$$

where $G_q=\{q(n)\}$ is a multiplicative semigroup with the partial order of $q(1)<q(2)<\cdots<q(n)<\cdots$ and $q(1)=1$, and $\Sigma_{m|q(n)/q(m)}$ covers all the terms which satisfy the relation of $q(n)/q(m)\in G_q$. In the pair potential approximation, the cohesive energy, $E_c(r)$, as a function of the distance between the nearest neighbor atoms for single-element crystal structure, can be expressed as the summation of radical pair potential as Eq. (1) through the reconstruction of structure-dependent coefficients $\{w(n),q(n)\}$. Therefore the pair potential can be obtained by LIM. The pair potentials between distinct atoms in a multi-element system can also be obtained by inverting the partial cohesive energies [30,38]. Indeed, one can obtain the pair potential between any two identical or different atoms by calculating and inverting the cohesive energies of the involved atom systems in real or virtual crystal structures. That is one of the advantages of LIM.

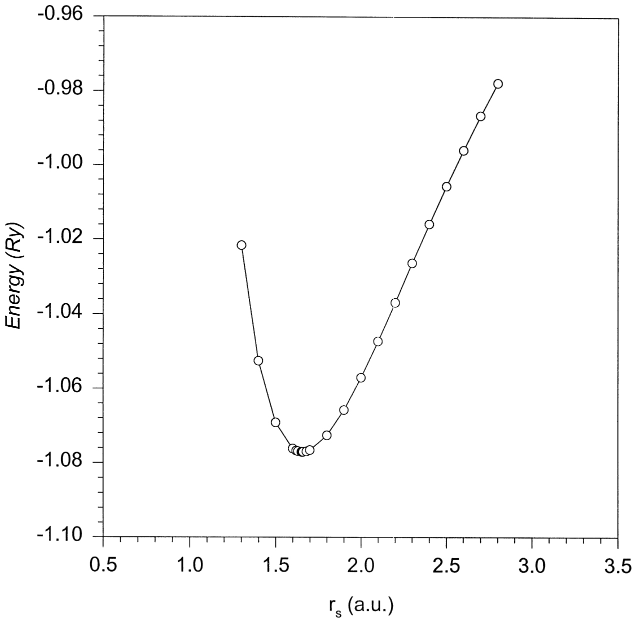

Fig. 1. Calculated total energy curve of fcc metallic hydrogen, where r_s is the Wigner–Seitz radius.

We use the TB-LMTO method [32] within the local density approximation (LDA) to calculate the cohesive energies of face-centered cubic (fcc) structure metallic hydrogen, transition metals Ti, Zr and Hf in hexagonal close-packed (hcp) structure and V, Nb and Ta in body-centered cubic (bcc) structure with the ‘‘frozen core’’ approximation, the Ceperley–Alder [33] exchange-correlation potential and the self-consistent scalar relativistic calculation. 240 k points, 140 k and 225 k points are used in irreducible wedges of fcc, bcc and hcp Brillouin zone respectively. As an example, the total energy curve of fcc metallic hydrogen are plotted in Fig. 1. The current TB-LMTO calculations shown in Table 1 are in fairly reasonable agreement with previous calculations using FLAPW method [34]. Since it is well known that the total energy of isolated atoms is not exactly described by the LDA, we shifted the computed cohesive energies of these metals, so that the absolute minimum of the cohesive energies coincide with the experimental equilibrium cohesive energies. For the inversion of pair potentials between metal and hydrogen atoms, the cohesive energy curves of the fully stoichiometric metal dihydrides TiH_2, ZrH_2 and HfH_2 in the cubic fluorite structure and VH_2, NbH_2 and TaH_2 in fcc structure are also calculated. The inverted pair potentials fitted in the form of the Rose model [35],

$$\phi(r)=-p_0(1+\alpha(r-r_0))\,\mathrm{e}^{-\alpha(r-r_0)}, \tag{4}$$

are tabulated in Table 2. In order to determine the atomic forces for the calculation of elastic constants and phonon spectrum, and for molecular-dynamics simulations, we adopt a ‘‘smooth’’ treatment in our fitting procedure by shifting the above pair potential function at the cutoff r_{cut} as

$$\phi_{\mathrm{smooth}}(r)=\phi(r)-\phi(r_{\mathrm{cut}})+(r_{\mathrm{cut}}-r)\phi'(r_{\mathrm{cut}}), \tag{5}$$

Table 1
The calculated equilibrium Wigner–Seitz radius r_0, total energy E_0, and bulk modulus B of FCC metallic hydrogen

	r_0(a.u.)	E_0(Ry)	B(Mbar)
TB-LMTO (present)	1.656	−1.0770	1.214
FLAPW (A.J. Freeman et al.) [34]	1.683	to 1.0763	1.251

Table 2
The fitted parameters of inverted pair potentials in the metal hydride systems

Name	p_0(eV)	α (Å^{-1})	r_0 (Å)
H–H	0.141	1.771	2.445
Ti–Ti	1.437	1.014	3.412
Zr–Zr	1.445	1.263	3.487
Hf–Hf	1.653	1.215	3.478
V–V	0.690	1.616	3.049
Nb–Nb	1.232	1.449	3.279
Ta–Ta	1.272	1.509	3.255
Ti–H	0.153	2.264	2.377
Zr–H	0.039	2.286	2.810
Hf–H	0.155	3.000	2.310
V–H	0.386	1.815	2.523
Nb–H	0.505	1.634	2.715
Ta–H	0.411	1.998	2.537

where $\phi'(r)$ is the first derivative of $\phi(r)$. The cutoff distance, r_{cut}, is set to be 6.5 Angstrom.

In general, because of the anisotropic property of hcp structure, the lattice constants, *a* and *c*, should be varied independently in the total energy calculation, and consequently one will get the total energy surface, $E(a,c)$. Because the inversion from the Eq.,

$$E(a,c) = \frac{1}{2} \sum_{\mathbf{r} \in \mathrm{latt}} \phi(|\mathbf{r}|), \tag{6}$$

can not yet be performed for two independent lattice constants, we keep the ratios, c/a, to be the experimental values of hcp metals in our calculations, and obtain the pair potentials of Ti, Zr and Hf by inverting the cohesive energy curve $E(a)$. To check the validity of this approach, we recalculate the contour plots of cohesive energies against lattice constants *a* and *c* using the inverted pair potentials. As an example, the inverted pair potential of Zr can be seen to well reproduce the stable hcp structure (Fig. 2). There is only one minimum in the contour plot which corresponds to the equilibrium structure. The calculated energy difference of Zr between fcc and hcp structures is 0.006 eV/atom, showing that the hcp phase is more stable consistent with the experimental observation.

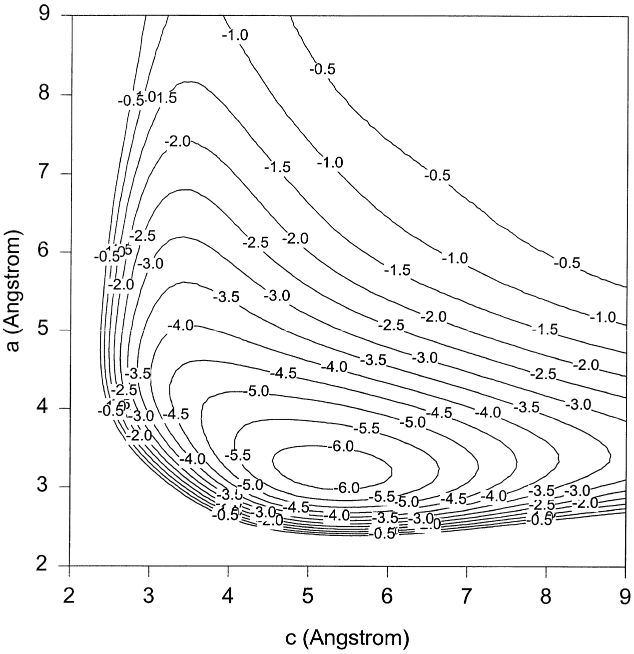

Fig. 2. Contour plot of cohesive energy versus lattice constants *a* and *c* of Zr in hcp structure.

3. Applications and discussions

By using the inverted pair potentials in Table 2, we can now carry out atomistic calculation of mechanical and thermal properties of these hydride systems. Because of our special interest in zirconium system in this paper [6–9], zirconium and zirconium hydride are discussed in detail. Some results for other systems are also listed.

The elastic constants can be calculated from the second derivative of total energy versus strains, namely,

$$C_{\alpha\beta} = \frac{1}{v_0} \frac{\partial^2 E}{\partial \epsilon_\alpha \, \partial \epsilon_\beta}, \tag{7}$$

where E is the total energy per atom, v_0 is the equilibrium atomic volume and $\{\epsilon_\alpha\}$ are the components of strain tensor. In the pair potential approximation, E can be expressed as a summation of pair potentials as in Eq. (6), then the elastic constants can be calculated from the pair potentials [36]. In Table 3, we compare the calculated elastic constants and equilibrium properties of the transition metals with the experimental data.The calculated results are in good agreement with the experimental data except the C_{44} of bcc metals V, Nb and Ta. Because C_{44} measures the elastic stiffness in the shear deformation mode, where the non-central interaction is important especially for non close-packed structures such as bcc, the central pair potential models are generally not suitable for these cases. For the metal hydride systems discussed in this paper, because of the quasi-ionic bond properties between hydrogen and metal atoms, the pair potential model may be a good approach. Table 4 is the calculated elastic constants of the metal hydrides. Because of the experimental difficulties, few experimental data of elastic constants of these systems exist. One available experimental value is the bulk modulus of ZrH_2, 0.855 (10^{11} N m^{-2}) [43]. Since the experimental value was measured at room temperature, the present value, 0.914 (10^{11} N m^{-2}) for $T = 0$ (K), is acceptable.

Though the central pair potential is not a very good description of the interatomic interactions in pure transition metals, the ab initio inverted pair potentials have been successfully used to calculate the elastic constants and some thermodynamic properties of the binary alloys [37,38]. The calculated elastic constants in Tables 3 and 4

Table 3
Some calculated properties of HCP Ti, Zr and Hf, and BCC V, Nb, Ta by the ab initio inverted pair potentials. The corresponding experimental values are listed in italics for comparison, and the lower numbers are the calculated values

	Ti	Zr	Hf	V	Nb	Ta
a_0 (Å) [41]	*2.950*	*3.230*	*3.190*	*3.030*	*3.300*	*3.300*
	2.951	3.226	3.185	3.033	3.390	3.371
c_0 (Å) [41]	*4.680*	*5.150*	*5.050*	–	–	–
	4.688	5.215	5.106	–	–	–
E_c (eV/atom) [41]	*4.850*	*6.250*	*6.440*	*5.310*	*7.570*	*8.100*
	5.021	6.232	6.587	5.310	7.570	8.100
B (10^{11} N m^{-2}) [42]	*1.0981*	*0.9716*	*1.1047*	*1.5400*	*1.5917*	*1.9421*
	0.9412	0.8867	0.9938	1.5704	1.7303	1.9325
C_{11} (10^{11} N m^{-2}) [42]	*1.7587*	*1.5518*	*1.8986*	*1.9600*	*2.3474*	*2.6632*
	1.7592	1.6806	1.8508	1.7922	2.0345	2.2470
C_{12} [42]	*0.8678*	*0.6712*	*0.7440*	*1.3300*	*1.2139*	*1.5816*
	0.5868	0.5583	0.6145	1.4594	1.5782	1.7754
C_{13} [42]	*0.6821*	*0.6451*	*0.6542*	–	–	–
	0.5015	0.4038	0.4818	–	–	–
C_{33} [42]	*1.9026*	*1.7227*	*2.0414*	–	–	–
	1.7747	1.8883	2.0883	–	–	–
C_{44} [42]	*0.5074*	*0.3626*	*0.5992*	*0.6700*	*0.2828*	*0.8736*
	0.5015	0.4038	0.4818	1.4594	1.5782	1.7897

show that the Cauchy relations ($C_{12} = C_{44}$ for cubic structure, and $C_{12} = C_{66}$ and $C_{13} = C_{44}$ for tetragonal and hexagonal structure), which are the strict results of central pair potentials, are indeed obeyed. The restriction due to the Cauchy relation is one of the major problems in the application of the pair potential models in transition metals. The pair potentials can well describe the interatomic interactions for most of the ionic crystals due to the Coulombic interaction, as a result of the strong charge transfer between atoms. Similarly, the charge transfer between different atoms in intermetallics due to the difference in electronegativity between distinct atoms accounted for the successful calculations of elastic properties using the inverted pair potentials [37,38]. The charge transfer between different atoms in a system is, to some extent, one of the criteria of the reasonable application of pair potentials. The successful applications of central pair potentials in ceramics is another example [12]. Recently, a central pair potential constructed on the basis of the generalized pseudopotential theory was also used to discuss the anisotropic migration of point defects in HCP Zr [39]. In metal hydrides, the charge transfer between hydrogen and metal atoms is obvious. The ab initio pair potentials obtained in this paper may be useful in explaining the mechanical properties of these metal hydrides, even though the pair potentials may not fulfil atomistic calculations for all physical properties. The calculated elastic constants in Table 4 are to be compared with experimental measurements.

Table 4
The calculated elastic constants of hydrides in the unit of 10^{11} N m^{-2}

	TiH_2	ZrH_2	HfH_2	VH_2	NbH_2	TaH_2
C_{11}	0.9933	0.7299	1.9102	2.6427	2.8361	3.0842
C_{12}	1.0285	1.0054	1.5556	1.0787	1.1319	1.4578
C_{13}	1.0359	1.1775	1.6915	–	–	–
C_{33}	1.0398	0.7786	1.6576	–	–	–
C_{44}	1.0359	1.1775	1.6915	1.0787	1.1319	1.4578
C_{66}	1.0285	1.0054	1.5556	–	–	–
B exp.	–	0.855	–	–	–	–
cal.	1.0310	0.9140	1.7059	1.6001	1.7000	2.0000

Fig. 3 is the contour plot of the cohesive energy as a function of a and c of stoichiometric ZrH_2 (ϵ phase). There is a region near the equilibrium structure where the energy difference is very small with different ratio c/a, and small nonhydrostatic stress could change the ratio c/a and induce structure transformation from $c/a = 0.682$ to

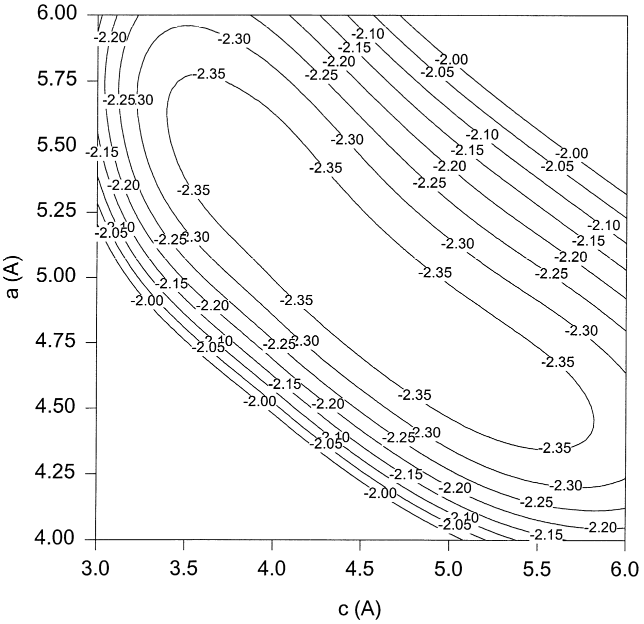

Fig. 3. Contour plot of cohesive energy versus lattice constants a and c of ZrH_2 in fct structure.

$c/a = 1.204$ approximately. This may provide the reason for stress induced twining in ϵ phase. This result is similar to a recent first-principle calculation [40], in which two stable structures ($c > a$ and $c < a$) are predicted and the $c > a$ structure is slightly more stable, but the fact is that $c > a$ structure is not observed in experiment.

Fig. 4 is the phonon dispersion curve of HCP Zr. The calculated acoustic phonons are in reasonable agreement with the experimental data. However, the calculated frequencies of the optical branches are much overestimated. The experimental data were measured at 300–1000 K. The anomalous softening of high frequency optical modes are related to the detailed topology of the Fermi surface existed in these anisotropic HCP metals [21]. This phenomenon can not be predicted by direct phonon spectrum calculations within the interatomic potential scheme. This may be one of the main reasons for the large discrepancies between the calculated and experimental values of optical modes.

The difference between the thermal expansion of transition metals and their hydrides is of interest because this difference may cause fracture and structural change (e.g. δ to γ hydride) during temperature cycling. Using the ab initio inverted pair potentials, we calculate the linear thermal expansion coefficients of these transition metals and their hydrides. Fig. 5 is the calculated linear thermal expansion coefficients of the transition metal Zr and its hydride. The calculated results of the metals are in good agreement with the experimental data at low temperature, while in the high temperature regime, experimental and calculated data are not comparable because of the exist of phase transition. It is noteworthy that there is a crossover point (near 360 K for Ti–H and Zr–H systems, and near 630 K for V–H and Nb–H systems) at which the values of linear thermal expansion coefficient of the hydride become larger than that of the corresponding metal. Because of the crossover point, the metal–hydrogen system may experience a stress induced structural transition or even fracture during temperature transients.

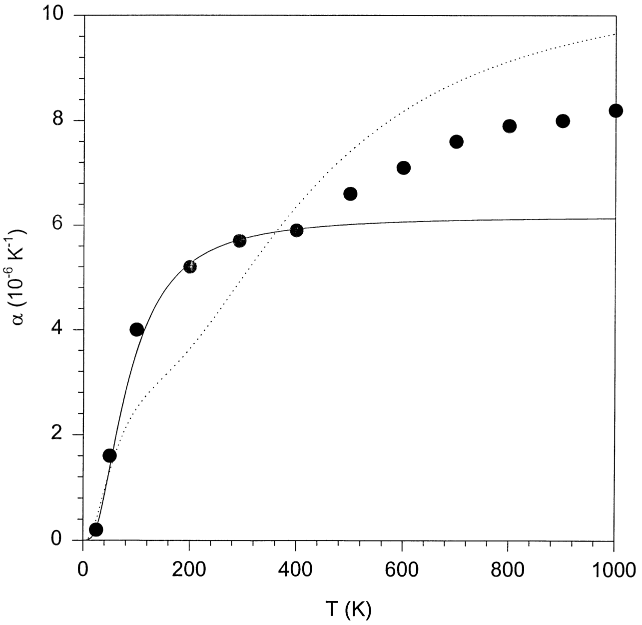

Fig. 5. The comparison of calculated linear thermal expansion coefficients of transition metal Zr (solid line) and its hydride (dotted lines). The dots are the experimental data for Zr [44].

To summarize, we obtained the effective pair potentials in some metal hydrides and performed the atomistic calculations of some mechanical and thermal properties of these hydrides. The present calculations illustrated the advantages and shortcoming of the ab initio inverted pair

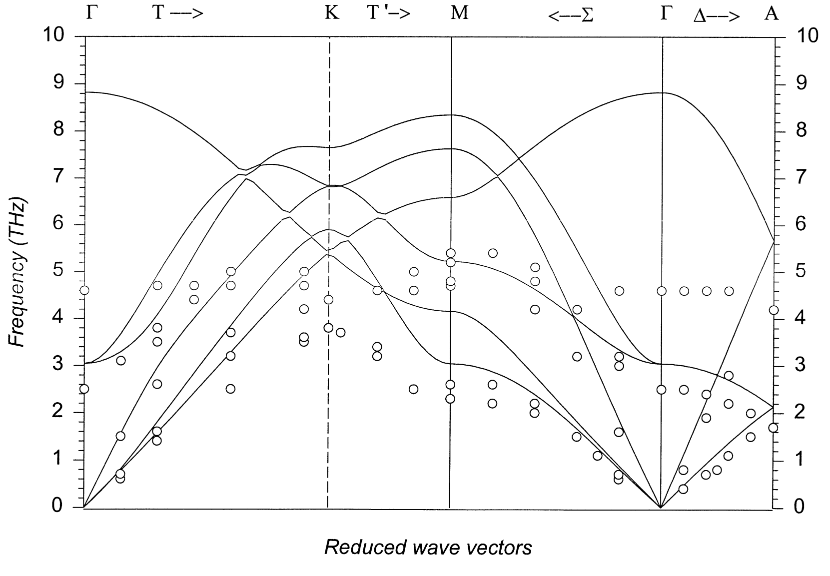

Fig. 4. The comparison of experimental and calculated phonon dispersions of hcp Zr. The circles are experimental values and the lines are calculated results.

potentials for the metal hydride systems. This is the first theoretical quantitative estimate of elastic constants, thermal expansions of these hydrides.

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