VOLUME 76, NUMBER 15 PHYSICAL REVIEW LETTERS 8 APRIL 1996

Free Energy Contributions to the hcp-bcc Transformation in Transition Metals

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(Received 21 July 1995)

The electronic and vibrational free energies of some hcp and bcc transition metals are computed *ab initio*. The vibrational part is obtained from a total-energy calculation over lattices with atoms randomly displaced according to a Gaussian distribution. The relative importance of electronic and vibrational excitations in the stabilization of the high-temperature bcc structure is clarified.

PACS numbers: 64.70.Kb, 65.50.+m, 71.10.–w, 71.15.Nc

An *ab initio* account of the relative stability of solid phases with different crystal structures, expressed as a Gibbs energy difference ΔG, is a major goal in current research. For transition metals in fcc, hcp, and bcc lattice structures, the previous apparent discrepancy in some systems (e.g., W) between *ab initio* and semiempirical ("experimental") ΔG at zero kelvin has been recently resolved [1,2]. Thus there is no doubt that first-principle electronic structure calculations yield reliable results for $\Delta G(T = 0\ \mathrm{K})$. Contrasting this progress, little has been done to provide $\Delta G(T)$ *ab initio* at finite temperatures. The main problem is to describe simultaneously and with equal accuracy the thermal excitations of the electronic degree of freedom and the phonons, including anharmonicity. While the electronic part ΔG_{el} is fairly straightforward to calculate also for transition metals [3,4], the phonons present a major difficulty. A simple approach is to relate Debye temperatures to *ab initio* calculated bulk moduli [5]. Detailed information on the phonon spectrum could be obtained *ab initio* through "frozen phonon" calculations [6], where, in principle, softening of special modes could be followed as a function of T and volume. But that would be too demanding for a systematic comparison of the vibrational part ΔG_{vib} for a large group of transition metals. Here we shall use an approach [7] that in certain aspects resembles frozen phonon calculations, but relies on an averaging procedure over the phonon spectrum that makes the calculation of ΔG_{vib} tractable. We calculate $\Delta G_{\mathrm{el}}(T)$ and $\Delta G_{\mathrm{vib}}(T)$ for Sc, Ti, V, Cr, Y, Zr, Nb, and Mo. The results are used to understand the high-T stabilization of the bcc phase in Sc, Ti, Y, and Zr, from a low-T hcp phase, and the stability of bcc V, Cr, Nb, and Mo at all temperatures.

The thermal electronic contribution to the Gibbs energy is computed using the linear-muffin-tin-orbital (LMTO) method with T as a variable [8–10]. The temperature-dependent equations for the total energy and thermal pressure can be found in Ref. [9]. Two different exchange-correlation energy functionals were used—the local density approximation (LDA) [11] and the generalized gradient approximation (GGA) [12]. As found in previous calculations [13], GGA agrees somewhat better than LDA with the experimental equilibrium volume and bulk modulus, in particular for the $3d$ metals. However, our conclusions concerning the T-dependent results (including the vibrational part) are the same using GGA and LDA. This Letter presents only the GGA results.

The electronic contribution $G_{\mathrm{el}} = E_{\mathrm{el}} + PV - TS_{\mathrm{el}}$ is obtained from an integration over $N(\epsilon)$, the density of states (DOS), where E_{el} is the total energy, P the pressure, V the volume, S_{el} the entropy, and all the quantities vary with the temperature T [8]. We neglect the electron-phonon many-body enhancement, which is important only at low temperatures ($T < \Theta_D/4$) [14]. Table I gives calculated results obtained with GGA potentials at 0 K along with the corresponding experimental values. For the hcp structure, the c/a ratio was fixed to 1.59 which is close to experimental data. The structures of all elements are correctly reproduced and the bcc-hcp structural energy differences do not differ from previous *ab initio* LDA results [17]. The values in Table I change as the temperature is raised because the free energy has an additional contribution from the entropy.

To understand the behavior of the electronic entropy we compare $N(\epsilon)$ of the bcc and hcp phases in Fig. 1, and recall that the entropy is roughly proportional to $N(\epsilon)$ within k_BT of E_F. For metals with few d electrons such as Ti and Zr, E_F is still within the low $N(\epsilon)$ region in the hcp phase, while in the bcc phase $N(E_F)$ is much larger. This fact will decrease the entropy term $-TS_{\mathrm{el}}$ faster for the bcc structure than for the hcp, and the total free energy differences between the two phases show a crossover at a

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TABLE I. Computed structural and ground-state properties. V_0 is the equilibrium volume and B_0 is the bulk modulus. Experimental volumes $V_{\rm exp}$ and bulk moduli $B_{\rm exp}$ are taken from Refs. [15,16].

Element	Structure	V_0 (a.u.^{3})	$V_{\rm exp}$ (a.u.^{3})	B_0 (kbar)	$B_{\rm exp}$ (kbar)	$V^{\rm hcp} - V^{\rm bcc}$ (a.u.^{3})	$E^{\rm hcp} - E^{\rm bcc}$ (mRy/atom)
Sc	hcp	171.8	168.7	533	558	-1.20	-3.9
Ti	hcp	121.3	119.1	1076	1050	0.89	-4.6
V	bcc	94.2	94.6	1761	1570	3.02	25.0
Cr	bcc	81.0	80.6	2454	1914	2.53	36.6
Y	hcp	227.0	222.9	369	366	-1.32	-5.1
Zr	hcp	162.5	157.1	884	965	2.35	-2.9
Nb	bcc	127.7	121.5	1616	1700	3.39	29.7
Mo	bcc	111.2	105.3	2321	2640	2.21	36.5

certain temperature T_s. A similar evaluation for Cr and Mo gives an opposite trend. The Fermi energy in the bcc phase is in a valley of $N(\epsilon)$ with small values of $N(E_F)$, while the hcp phase has a large $N(E_F)$ (see Fig. 1). Hence the entropy term will diminish the large difference between the free energies of the two phases, implying a transition from bcc to hcp at large T. However, the difference $\Delta G_{\rm el}(T = 0)$ between hcp and bcc structures is so large (36 mRy/atom) that the crossover in $G_{\rm el}$ can happen only at temperatures much above the melting temperature, at $P = 0$. In Cr and Mo $\Delta G_{\rm el}$ becomes smaller at high pressures.

Figure 2 shows the calculated zero-pressure electronic Gibbs energy $\Delta G_{\rm el}(T)$, the differences $\Delta E_{\rm el}(T)$ and $T\Delta S_{\rm el}(T)$ between the bcc and hcp structures as a function of temperature. Note that the energy scale differs for different elements. The hcp-bcc transition temperature T_s implied by the electronic contribution only is obtained from the intersection of $\Delta G_{\rm el}(T)$ with the zero energy axis. For Sc, Y, Ti, and Zr we get $T_s = 4300$, 4800, 2050, and 1500 K, respectively, from $\Delta G_{\rm el}(T) = 0$. This is larger than experimental values, but it is satisfactory to see that the relative variation of T_s among these elements follows experiment. The $G_{\rm el}(T)$ curves are rather flat at low T, and a small vertical shift of one of the curves relative to the other will considerably shift T_s. The present results indicate that the bcc lattice in Sc, Y, Ti, and Zr at very high T can be stabilized by electronic thermal excitations.

The method for thermal disorder is based on LMTO, but with the structure matrix averaged over various configurations and reduced to a form for a few atoms per cell. Vibrational disorder is obtained assuming that each atom has a displacement given by a Gaussian function with σ as

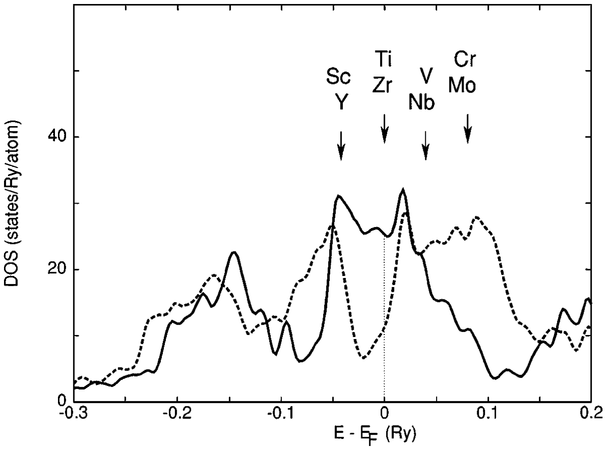

FIG. 1. (a) Density of states for bcc (solid line) and hcp (dotted line) Zr and qualitative indications of the Fermi level for the other metals.

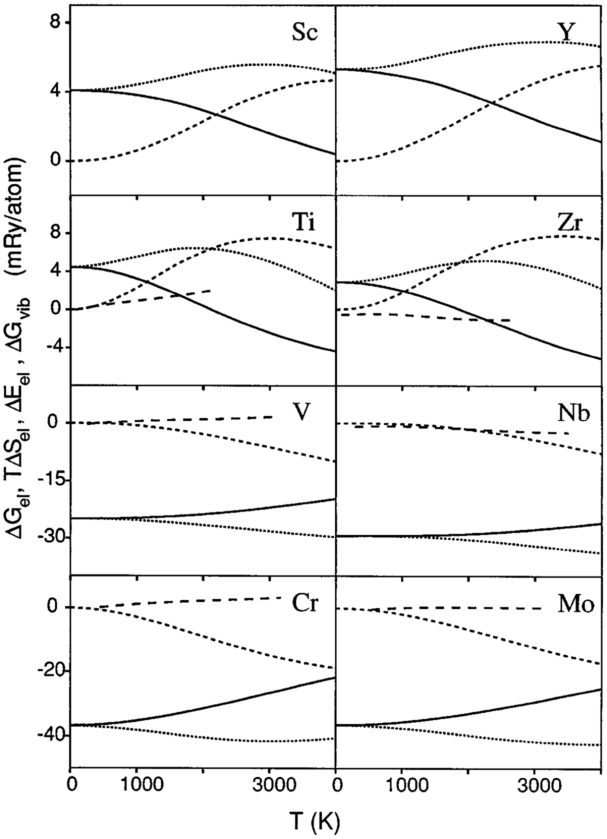

FIG. 2. The difference of the electronic Gibbs energy $\Delta G_{\rm el}$ (solid line), total energy $\Delta E_{\rm el}$ (dotted line), entropy term $T\Delta S_{\rm el}$ (dashed line), and vibrational Gibbs energy $\Delta G_{\rm vib}$ (long dashed line) between the bcc and hcp phases.

mean square displacement around the equilibrium position. The Gaussian distribution function is valid in the harmonic approximation and cubic symmetry, but we apply it also to the hcp lattice, and randomly generate atomic positions in large supercells, before the averaging of the structure matrix is done [7]. This method does not describe selected phonons but it deals with Gibbs energy differences of disordered structural configurations of hcp and bcc lattices.

The parameter of disorder σ is related to the temperature T. If the vibrations were harmonic, with $P = 0$ and at high temperatures ($T > \Theta_D$), σ and T would be related through $H_{\mathrm{vib}}(\sigma) - H_{\mathrm{vib}}(0) = \frac{3}{2}k_B T$. When H_{vib} includes anharmoncity, and does not vary as σ^2, we use the thermodynamic relation $dH = TdS + VdP$ to define a temperature T as

$$T = \left(\frac{\partial H_{\mathrm{vib}}}{\partial \sigma}\right)_P \left(\frac{\partial \sigma}{\partial S_{\mathrm{vib}}}\right)_P . \tag{1}$$

Then we use the classical (i.e., for $T > \Theta_D$) expression for the entropy, which contains σ (obtained through a phase-space-volume relation) and yields a term $\ln(\sigma^3)$, i.e., $(\frac{\partial S_{\mathrm{vib}}}{\partial \sigma})_P = \frac{3}{\sigma}$. These relations define completely the vibrational Gibbs energy $G_{\mathrm{vib}}(\sigma) = H_{\mathrm{vib}}(\sigma) - TS_{\mathrm{vib}}(\sigma)$ of both structures. Here we are mainly interested in results at $P = 0$. Therefore $G_{\mathrm{vib}}(\sigma)$ for each element has to be minimized with respect to the lattice parameter when σ is varied to correspond to a maximum T of a few thousand kelvin.

The difference between the vibrational Gibbs energies of bcc and hcp structures is given by

$$\Delta G_{\mathrm{vib}}(T) = H_{\mathrm{vib}}^{\mathrm{bcc}}(\sigma_{\mathrm{bcc}}) - H_{\mathrm{vib}}^{\mathrm{hcp}}(\sigma_{\mathrm{hcp}}) - T \ln \frac{\sigma_{\mathrm{bcc}}^3 V_{\mathrm{bcc}}}{\sigma_{\mathrm{hcp}}^3 V_{\mathrm{hcp}}} , \tag{2}$$

where $\sigma_{\mathrm{bcc}} = \sigma_{\mathrm{bcc}}(T)$ and σ_{hcp} refer to the degree of disorder at a given T for the corresponding phases. Our Gaussian ansatz allows for the thermal-expansion effect on the phonons in the quasiharmonic approximation, but it leaves out most of the other anharmonic effects. However, we are primarily interested in the difference ΔG_{vib} between two solid phases. If the additional anharmonic terms of the hcp and bcc phases are approximately equal, they will cancel in ΔG_{vib}.

Figure 2 shows (long dashed line) the computed $\Delta G_{\mathrm{vib}}(T)$ for Ti, V, Cr, Zr, Nb, and Mo. It is found that ΔG_{vib} is not the major cause in driving a low-temperature hcp structure to the high-temperature bcc phase, contrary to what is sometimes stated. However, ΔG_{vib} is of course important for the precise value of T_s since ΔG_{el} varies rather slowly with T near T_s. For V, Cr, Nb, and Mo, $\Delta G_{\mathrm{vib}}(T)$ is also very small compared to the $\Delta E_{\mathrm{el}}(T)$ term. In Sc and Y because of the higher fraction of delocalized electrons over localized $3d$ states, we do not get an equally accurate vibrational energy and we refrain from definite conclusions in that case. These examples show that the phase stability depends heavily on electronic energies, but a precise determination of the vibrational energy is needed for a quantitative description of the hcp-bcc transition temperature.

It is instructive to describe further the role of vibrational properties by computing a Debye temperature Θ_D and two different approaches are considered. First, the Debye temperature (Θ_D) is obtained through the computed vibrational energies $E(\sigma)$ and within a harmonic approximation of lattice vibrations, expressed as [7,18] $\Theta_D^a = \sqrt{\frac{5}{3}}\,\frac{\hbar}{k_B}\sqrt{\frac{1}{M}\,\frac{\partial^2 E(\sigma)}{\partial \sigma^2}}$. Θ_D^a is temperature dependent, both because of lattice dilatation and because of explicitly anharmonic interactions present also at fixed volume.

Second, the Debye temperature is evaluated as $\Theta_D^b = (\frac{3}{4\pi})^{1/6}\,\frac{h}{k_B}\sqrt{\frac{r_{\mathrm{WS}}B}{M}}$ where r_{WS} is the equilibrium Wigner-Seitz radius, M is the atomic weight, and B is the bulk modulus [19]. Moruzzi, Janak, and Schwarz [5] used the above expression multiplied by an empirical constant to estimate Θ_D for 14 nonmagnetic metals. It is not as good to use the bulk modulus to derive a Debye temperature that gives the low-temperature heat capacity, since then the shear modulus is the important elastic constant. However, we have found that the Debye temperature to be used in the high-temperature G_{vib} is well correlated to the bulk modulus B, in particular when one also makes a small correction depending on the Poisson number.

These two different approaches give very similar trends for all computed Debye temperatures except for Sc and Y, and they also compare very well with experimental values (see Table II). The estimated differences of Θ_D for both structures are very small (a few kelvin) for $4d$ metals and they are larger for $3d$ metals (20–30 K). Because ΔG_{vib} at high T depends only on the ratio of the Debye temperatures for the bcc and hcp structures these results confirm the picture that leads to a small ΔG_{vib}.

Neutron scattering data [21] for Ti show that $\Theta_D^{\mathrm{bcc}}/\Theta_D^{\mathrm{hcp}}$ is ≈ 0.9 at $T_s \approx 1156$ K of the hcp-bcc transition. However, if Θ_D^{hcp} is smoothly extrapolated to high temperatures [22], one finds for Ti that close to the melting temperature $T_m = 1933$ K, Θ_D^{bcc} is indeed somewhat larger than Θ_D^{hcp},

TABLE II. Theoretical and experimental Debye temperatures. Θ_D^a and Θ_D^b are obtained from our calculated vibrational energy and bulk modulus, respectively. Θ_D^S and Θ_D^{ela} are Debye temperatures derived from the entropy at 298 K, and from low-temperature data [16,20].

Element	Structure	Θ_D^a (K)	Θ_D^b (K)	Θ_D^S (K)	Θ_D^{ela} (K)
Sc	hcp	200	266	311	358
Ti	hcp	360	348	352	425
V	bcc	460	411	384	399
Cr	bcc	540	469	473	589
Y	hcp	140	165	211	256
Zr	hcp	255	238	244	296
Nb	bcc	320	307	282	277
Mo	bcc	360	354	380	474

in agreement with our calculation. The large S_{vib} (low Θ_D) of the bcc phase contributes significantly to make this phase thermodynamically more stable than the hcp phase only close to $T = T_s$. On approaching T_m, ΔG_{vib} of Ti decreases and even changes sign. Thus, if it were not for the very large ΔG_{el} obtained above, the hcp phase would again be more stable than the bcc phase. Similar results hold for Zr. The low Θ_D^{bcc} near T_s is known to be caused by the approach to a bcc lattice instability [6] at even lower T. For harmonic vibrations our σ leads to an average of $\omega^{-2}(\mathbf{q})$. The instability appears for only a small range of $\mathbf{q}$ vectors in the Brillouin zone. Other phonon modes are not much affected [21] and cause no problem in their contribution to σ. At high T, the unstable low-T modes become stable [21]. Then, and also because of their small weight (few $\mathbf{q}$ values) in $\omega^{-2}(\mathbf{q})$, our *ansatz* is adequate. Moreover, S_{vib} at high T depends on $\ln[\omega(\mathbf{q})]$. A logarithmic singularity is very weak and a phonon instability has a negligible effect on the total S_{vib} until one actually reaches $\omega(\mathbf{q}) = 0$ for a mode [2]. Thus we argue that even if some phonon modes become soft, it should not be serious in our approach.

In conclusion, we presented a unified *ab initio* approach to the electronic and vibrational parts of the free energy of transition metals. The method "turns off" lattice instabilities and thus is suitable to describe the thermodynamics of systems such as Ti and Zr where unstable lattice vibrations are stabilized at high T. It is found that the electronic thermal energy is more important than the vibrational energy in the stabilization of the bcc phase in Ti and Zr close to the melting temperature.

This work has been supported (E. G. M.) by the Swiss National Science Foundation and by the Swedish research councils NUTEK, NFR, and TFR.

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