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Homology of interatomic forces and Debye temperatures in transition metals

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Using experimental data on the entropy S at intermediate temperatures, corrected for an electronic term to get the vibrational entropy, we obtain well-defined and accurate "entropy Debye temperatures" $\Theta=\Theta^S$. From Θ^S we define a quantity with the dimension of a force constant, $k^S \equiv M(k_B\Theta/\hbar)^2$, where M is the atomic mass. Similarly, data on the low-temperature vibrational heat capacity and the elastic coefficients yield Debye temperatures Θ^C and Θ^{elas} and corresponding force constants k^C and k^{elas}. The ratios of k^S for the 4d-5d pairs Zr,Hf, Nb,Ta, Mo,W, Tc,Re, Ru,Os, Rh,Ir, and Pd,Pt are remarkably constant, $(k^S)^{4d}/(k^S)^{5d}=0.76\pm0.01$, in spite of varying crystal structures. Further, $(k^C)^{4d}/(k^C)^{5d}=0.70\pm0.07$ and $(k^{\text{elas}})^{4d}/(k^{\text{elas}})^{5d}=0.69\pm0.08$. The corresponding force-constant ratios k^{3d}/k^{4d} vary more. This correlates with an approximately constant atomic-volume ratio $\Omega^{4d}/\Omega^{5d}=0.99\pm0.02$, while $\Omega^{3d}/\Omega^{4d}=0.81\pm0.05$ shows irregularities, mainly of magnetic origin. As a basis for our analysis, we review low-temperature Debye temperatures Θ^{elas} and Θ^C and the bulk modulus B of the transition metals.

I. INTRODUCTION

The concept of homology refers to the predictable manner by which properties vary in chemically related substances. For instance, many properties of transition metals such as the cohesive energy, the bulk and shear modulus, the melting and boiling temperatures, the inverse thermal expansion coefficient, and the inverse atomic volume show the same general behavior for the 3d, 4d, and 5d series, i.e., a paraboliclike shape when plotted versus the group number in the Periodic Table.[1,2] In such plots it is noteworthy that the ratio Ω^{4d}/Ω^{5d} for the atomic volumes of two elements with the same group number, i.e., for the pairs Zr,Hf, Nb,Ta, Mo,W, Tc,Re, Ru,Os, Rh,Ir, and Pd,Pt, is approximately a constant, $\Omega^{4d}/\Omega^{5d}=0.99\pm0.02$. Along this d series, the crystal structure varies as hcp, bcc, bcc, hcp, hcp, fcc, and fcc. Another example of a striking universality is that recently found[3] for the equation of state of metals expressed in the bulk modulus, the cohesive energy, and the Wigner-Seitz radius. It is the purpose of this paper to explore the homology of quantities related to the interatomic forces in transition metals. In particular we consider a well-defined and accurately measurable quantity, a vibrational-entropy-related average interatomic force constant k^S, which has a remarkable constancy in the 4d-5d series: $(k^S)^{4d}/(k^S)^{5d}=0.76\pm0.01$. In previous work on, e.g., carbides, borides, and nitrides, k^S showed a similar regularity.[4] We will find that the corresponding 3d-4d ratios vary more than in the 4d-5d case. We shall also discuss the ratios $(k^i)^{4d}/(k^i)^{5d}$, and the corresponding 3d-4d relations, where k^i refers to force constants k^C, k^{elas}, and k^B derived from the low-temperature heat capacity, the elastic constants, and the bulk modulus, respectively. This leads us to a review of elastic-limit Debye temperatures and bulk moduli for transition metals.

II. FORCE CONSTANTS FROM THE VIBRATIONAL SPECTRUM

In a solid, the frequency spectrum can be characterized by frequencies $\omega(n)$ defined so that $[\omega(n)]^n$ is the average of ω^n, with $n>-3$. For $n=0$, $\omega(0)$ is defined from the average of $\ln(\omega)$. It is convenient to represent $\omega(n)$ by Debye temperatures $\Theta(n)$ defined as $\Theta(n) \equiv(\hbar/k_B)[(n+3)/3]^{1/n}\omega(n)$. When $n=0$ we take $\Theta(0)=(\hbar/k_B)\exp(\frac{1}{3})\omega(0)$. This definition has the advantage that when the frequency spectrum is of the Debye type, all $\Theta(n)$ become equal, $\Theta(n)=\Theta_D$. Also, in the limit $n\rightarrow-3$, $\Theta(-3)$ equals the ordinary Debye temperature Θ^{elas}.

Let $C(T)$ and $S(T)$ be the heat capacity and the entropy as a function of the temperature T for a certain spectrum of harmonic vibrations in a solid. For each T, we can put the true $C(T)$ and $S(T)$ equal to the result of a Debye model and hence define a "heat-capacity Debye temperature" $\Theta^C(T)$ and an "entropy Debye temperature" $\Theta^S(T)$. The Debye temperatures $\Theta(n)$ are related to certain limits of Θ^C and Θ^S. When $T\rightarrow0$, $\Theta^C(0)=\Theta^S(0)=\Theta(-3)$. In the limit of high temperatures ($T=\infty$ or, rather, $T/\Theta\gg1$), $\Theta^C(\infty)=\Theta(2)$ and $\Theta^S(\infty)=\Theta(0)$.

Here we shall be interested in $\Theta(0)$ derived from the vibrational entropy $S_{\text{vib}}(T)$ through the following procedure, which has been described elsewhere.[5] Let S_{tot} be the measured total entropy and S_{el} the entropy of the

TABLE I. The Debye temperatures Θ^i (K) and the corresponding force constants k^i (N/m), with $i = S, C$ or elas, as derived from (S) the standard entropy at 298 K, from (C) the low-temperature heat capacity, and from (elas) the low-temperature elastic constants.

	Ti		V		Cr		Mn		Fe		Co		Ni	
	Θ	k	Θ	k	Θ	k	Θ	k	Θ	k	Θ	k	Θ	k
S	352	169	384	214	473	331	358	200	413	271	365	223	378	239
C	429	251	400	232	598	529	409	262	477	362	460	355	477	380
elas	425	246	399	231	589	513	409	262	478	363	453	344	476	378

	Zr		Nb		Mo		Tc		Ru		Rh		Pd	
	Θ	k	Θ	k	Θ	k	Θ	k	Θ	k	Θ	k	Θ	k
S	244	154	282	210	380	394	320	286	384	424	344	346	269	219
C	299	232	277	203	470	603	454	575	555	886	489	700	275	229
elas	296	227	277	203	474	613	449	562	554	883	489	700	276	231

	Hf		Ta		W		Re		Os		Ir		Pt	
	Θ	k	Θ	k	Θ	k	Θ	k	Θ	k	Θ	k	Θ	k
S	203	209	229	270	319	532	264	369	320	554	286	447	228	287
C	252	323	258	343	380	756	416	917	467	1181	425	988	237	312
elas	253	325	264	359	384	772	416	917	467	1181	430	1011	238	314

conduction electrons. $S_{\text{vib}} = S_{\text{tot}} - S_{\text{el}}$ yields an entropy Debye temperature $\Theta^S(T)$ which at intermediate and high temperatures varies slowly with T and includes the anharmonic phonon frequency shifts to low order in perturbation theory. Already at $T > \Theta^S/2$, $\Theta^S(T)$ gives a very good approximation of $\Theta(0)$. It is advantageous not to consider T too high, where anharmonic effects give rise to a substantial temperature dependence in $\Theta^S(T)$. S_{el} is taken as $\gamma T/(1+\lambda)$, where γT is the low-temperature electronic heat capacity and $1+\lambda$ is an electron-phonon enhancement factor,[6] present only at low T.

From our room-temperature value of Θ^S we define a quantity k^S with the dimension of a force constant, $k^S \equiv M(\hbar\Theta^S/k_B)^2$. Similarly, we define force constants $k^C = M(\hbar\Theta^C/k_B)^2$ and $k_{\text{elas}} = M(k_B\Theta^{\text{elas}}/\hbar)^2$ from the Debye temperatures Θ^C and Θ^{elas} which are obtained from the low-temperature limit of the heat capacity and the elastic coefficients c_{ij}, respectively. Within this definition, all the force constants are equal for a strict Deybe spectrum. Table I gives our results. The total uncertainty in k^S typically is $\leq 2\%$, corresponding to an uncertainty $\leq 1\%$ in the experimentally determined S_{tot}. Θ^C and Θ^{elas} each measure the same quantity $\Theta(-3)$ defined above. Differences between them in Table I reflect the uncertainty in Θ. We note that with the exception of Nb, all $\Theta^S < \Theta^C$.

III. A REVIEW OF DEBYE TEMPERATURES AND BULK MODULI

The values of Table I are from the following sources, if no other reference is given in the list below: Θ^S is based on the standard entropy ${}^0S = S_{\text{tot}}(298.15\text{ K})$ from SGTE.[7] We have not corrected Θ^S for the magnetic entropy[8] due to spin disorder at 298 K in Cr, Mn, Fe, Ni, and Co. For Θ^C we mainly rely on a compilation by Phillips.[9] Most Θ^{elas} for cubic metals are from Verma and Aggarwal.[10] The bulk moduli B in Table II are mostly from single-crystal elastic constants c_{ij} at room temperature, compiled by Hearmon[11] in the Landolt-Börnstein tables. When various sources suggest very different values, we have used the following guidelines: There should be no large difference between Θ^C and Θ^{elas}, and the selected quantities should fit reasonably the trend shown by neighboring elements. Since there is more consensus on the entropy, we have preferred results which show the same trend as Θ^S. The following list gives comments, and references other than those mentioned above. For manganese and osmium, there has been considerable disagreement on Θ and B, and we discuss these metals in some detail.

Titanium. Our Θ^C, from Phillips,[9] agrees well with $\Theta^C = 425 \pm 5$ K from Desai.[12] Θ^{elas} from Singh and Tolpadi.[13]

Vanadium. Θ^S from ${}^0S = 29.708 \pm 0.08$ J/mol K, given by Desai.[14]

Chromium. Θ^C from Gschneidner.[1] Phillips[9] has $\Theta^C = 600$ K. Our Θ^{elas} is from Ref. 10. White *et al.*[15] prefer $\Theta^{\text{elas}} = 577$ K, obtained in a private communication from J. G. Collins (1985).

Manganese. Θ^S from ${}^0S = 32.22 \pm 0.1$ J/mol K, given by Desai.[16] The information on Θ^C and Θ^{elas} is meager. Our Θ^C, from Guthrie *et al.*,[17] is based on an analysis by them of their own data in the liquid-helium range together with data by Booth *et al.*[18] in the liquid-hydrogen range. Our Θ^C agrees with that of Stewart[19] and is within the limits $\Theta^C = 418 \pm 32$ K selected by Gschneidner,[1] but is higher than the value $\Theta^C = 385$ K selected by Phillips[9] from data by Shinozaki *et al.*[20] We note that early measurements by Elson *et al.*,[21] $\Theta^C = 410$ K, by Armstrong and Grayson-Smith,[22] $\Theta^C = 417$ K, and by Franzosini *et al.*,[23] $\Theta^C = 415$ K, are consistent with our choice. Lacking detailed information on c_{ij} we take $\Theta^{\text{elas}} = \Theta^C$. Our B is from high-pressure x-ray diffraction by Takemura *et al.*[24] Early static measurements by Bridgman,[25] after being reanalyzed by Slater[26] and Birch,[27] gave

TABLE II. Selected values of the bulk modulus B (GPa).

Ti	V	Cr	Mn	Fe	Co	Ni
105	157	160	131	167	187	184
Zr	Nb	Mo	Tc	Ru	Rh	Pd
95	170	264	281	311	267	188
Hf	Ta	W	Re	Os	Ir	Pt
109	193	310	365	410	355	283

$B=125$ GPa. Later data by Bridgman,[28] analyzed by Gilvarry,[29] gave $B=59.5$ GPa. However, the analysis by Slater and Birch gives $B'=(\partial B/\partial P)_T \cong 13$, which falls outside the range $2<B'<7$ covered by the data for most elements.[30] We have therefore analyzed the more recent data by Bridgman,[28] using the Murnaghan model and allowing B and B' to vary freely. We found that a good fit to the V versus P data leads to large B' ($\cong 19$). The analysis by Gilvarry[29] was based on a polynomial representation of the $\Delta V/V$ versus P relation. We have analyzed Bridgman's data using a $\Delta V/(PV)$ versus P plot. Considerable deviation from the linear behavior described by $-\Delta V/V=aP+bP^2$ is observed. However, the results by Gilvarry were reproduced when the points from the lowest pressure range ($P<3$ GPa) were excluded. We conclude that the data of Bridgman[28] may not be quite accurate. Rosen[31] reported $B=92$ GPa from ultrasonic measurements in polycrystalline Mn from 4.2 to 300 K. Possible explanations of the discrepancy with our adopted value are given in Ref. 24. We note that $\Theta^{\mathrm{elas}}=485$ K, obtained by Rosen,[31] is also in disagreement with the available Θ^C; see above.

Iron. Θ^{elas} from Singh and Tolpadi.[13]

Cobalt. Θ^{elas} from Wolcott.[32]

Nickel. Θ^C from Stewart,[19] which is consistent with $\Theta^C=472\pm5$ K selected by Desai.[33]

Zirconium. Θ^C from Fernández Guillermet[34] and Θ^{elas} from Fisher and Renken.[35] B from an analysis by Fernández Guillermet[34] of data by Fisher and Renken.[35]

Niobium.

Molybdenum. Our Θ^C (from Phillips[9]) is also consistent with $\Theta^C=459\pm10$ K proposed by Gschneidner[1] but higher than $\Theta^C=430\pm20$ K, preferred in the review by Desai.[16] We note, however, that the most recent information tabulated by Desai[16] (cf. his Table 8) suggests a higher Θ value. The value $B=282$ GPa, from Fernández Guillermet,[36] results from a Murnaghan analysis of compression data and is probably too high, due to the low value $(\partial B/\partial P)_T=3.25$ needed to fit the P-V data in the shock-wave range.

Technetium. Θ^C from Trainor and Brodsky.[37] Θ^S, Θ^{elas}, and B are discussed by Fernández Guillermet and Grimvall.[38] That work makes use of relation (2a) to estimate ${}^0S$, but the estimate is consistent with other thermodynamic data for Tc.

Ruthenium. Θ^{elas} from Singh and Tolpadi.[13]

Rhodium. Θ^{elas} from Walker *et al.*[39] The information on Θ^C is old and conflicting. Clusius and Gutiérrez Losa[40] reported $\Theta^C=450$ K, Wolcott[41] $\Theta^C=478$ K, and Budworth *et al.*[42] $\Theta^C=512\pm17$ K. Gschneidner[1] and Phillips[9] proposed different averages, $\Theta^C=480\pm32$ and $\Theta^C=500$ K, respectively, whereas Stewart[20] preferred the value of Budworth *et al.*[42] All the experimental Θ^C values differ from our Θ^{elas} by more than 10 K, which seems to be too large a difference. We therefore adopted $\Theta^C=\Theta^{\mathrm{elas}}$, which falls within the experimental scatter band and is bracketed by the averages proposed in previous reviews.

Palladium. Θ^C from Furukawa *et al.*[43]

Hafnium. Θ^C from Stewart[19] and Θ^{elas} from Singh and Tolpadi.[13]

Tantalum.

Tungsten. Θ^S from Grimvall *et al.*[44]

Rhenium. Θ^C from Smith and Keesom[45] and Θ^{elas} from Shepard and Smith.[46]

Osmium. Θ^C from Stewart.[19] Lacking detailed information on c_{ij}, we take $\Theta^{\mathrm{elas}}=\Theta^C$. B is estimated in the present work from a consideration of the $(k^B)^{4d}/(k^B)^{5d}$ versus number of d electrons curve. A linear interpolation was performed between the $(k^B)^{4d}/(k^B)^{5d}$ values for Tc,Re and Rh,Ir, which is suggested by the smooth corresponding variation in the Ω^{4d}/Ω^{5d} and $(k^S)^{4d}/(k^S)^{5d}$ ratios for Tc,Re, Ru,Os, and Rh,Ir. Gschneidner[1] considered an empirical relation between the cohesive energy and B, and estimated $B=418$ GPa. Our adopted value is, however, independent of thermal data from very high temperatures (e.g., enthalpy-of-melting data) which are lacking for Os (cf. our discussion in Ref. 38). Köster and Franz[47] estimated $B=373$ GPa. From empirical trends in B versus the atomic volume, Kempter[48] estimated $B=336$ GPa, which is much lower than our value.

Iridium. Θ^C from Gschneidner.[1] Phillips[9] selects a slightly lower value, $\Theta^C=420$ K. Our Θ^{elas}, from Ref. 10, is slightly lower than $\Theta^{\mathrm{elas}}=436\pm2$ K suggested by MacFarlane *et al.*[49] B is from MacFarlane *et al.*[49] Purwins *et al.*[50] give $B=370$ GPa.

Platinum. Θ^C from Stewart.[19]

IV. HOMOLOGY OF FORCE CONSTANTS

There is a close correlation between k^S of the $4d$ and $5d$ series and a weaker correlation between the corresponding elastic-limit force constants k^{elas}, Fig. 1. In order to investigate such correlations further we form the ratios k^{3d}/k^{4d} and k^{4d}/k^{5d} for each group in the Periodic Table, from the pair Ti,Zr to Ni,Pt and from Zr,Hf to Pd,Pt, Table III. The ratios (1d) and (2d) are obtained from our definition $k^B \equiv \Omega^{1/3}B$, where B is the bulk

TABLE III. Ratio of the atomic volumes Ω, the effective force constants k^i ($i=S$, C, elas, B), and the quantity $E''=E_{\text{coh}}/\Omega^{2/3}$.

	Ti,Zr	V,Nb	Cr,Mo	Mn,Tc	Fe,Ru	Co,Rh	Ni,Pd
Ω	0.86	0.77	0.77	0.85	0.87	0.80	0.74
S	1.10	1.02	0.84	0.70	0.64	0.64	1.09
C	1.08	1.14	0.88	0.45	0.41	0.51	1.66
elas	1.08	1.14	0.84	0.47	0.41	0.49	1.64
B	1.05	0.85	0.56	0.44	0.51	0.65	0.89
E''	0.86	0.83	0.71	0.47	0.70	0.88	1.39
	Zr,Hf	**Nb,Ta**	**Mo,W**	**Tc,Re**	**Ru,Os**	**Rh,Ir**	**Pd,Pt**
Ω	1.04	1.00	0.98	0.97	0.97	0.97	0.98
S	0.74	0.78	0.74	0.77	0.76	0.77	0.76
C	0.72	0.59	0.80	0.63	0.75	0.71	0.73
elas	0.70	0.57	0.79	0.61	0.75	0.69	0.74
B	0.88	0.88	0.85	0.76	0.75	0.74	0.66
E''	0.94	0.93	0.77	0.87	0.84	0.84	0.68

modulus. The average ratios are (with standard deviation)

$$(k^S)^{3d}/(k^S)^{4d}=0.86\pm0.2\ , \tag{1a}$$

$$(k^C)^{3d}/(k^C)^{4d}=0.87\pm0.4\ , \tag{1b}$$

$$(k^{\text{elas}})^{3d}/(k^{\text{elas}})^{4d}=0.87\pm0.4\ , \tag{1c}$$

$$(k^B)^{3d}/(k^B)^{4d}=0.71\pm0.2\ ; \tag{1d}$$

$$(k^S)^{4d}/(k^S)^{5d}=0.76\pm0.01\ , \tag{2a}$$

$$(k^C)^{4d}/(k^C)^{5d}=0.70\pm0.07\ , \tag{2b}$$

$$(k^{\text{elas}})^{4d}/(k^{\text{elas}})^{5d}=0.69\pm0.08\ , \tag{2c}$$

$$(k^B)^{4d}/(k^B)^{5d}=0.79\pm0.08\ . \tag{2d}$$

The constancy of the k^S ratios for the $4d$-$5d$ pairs is remarkable, in particular since the crystal structure varies

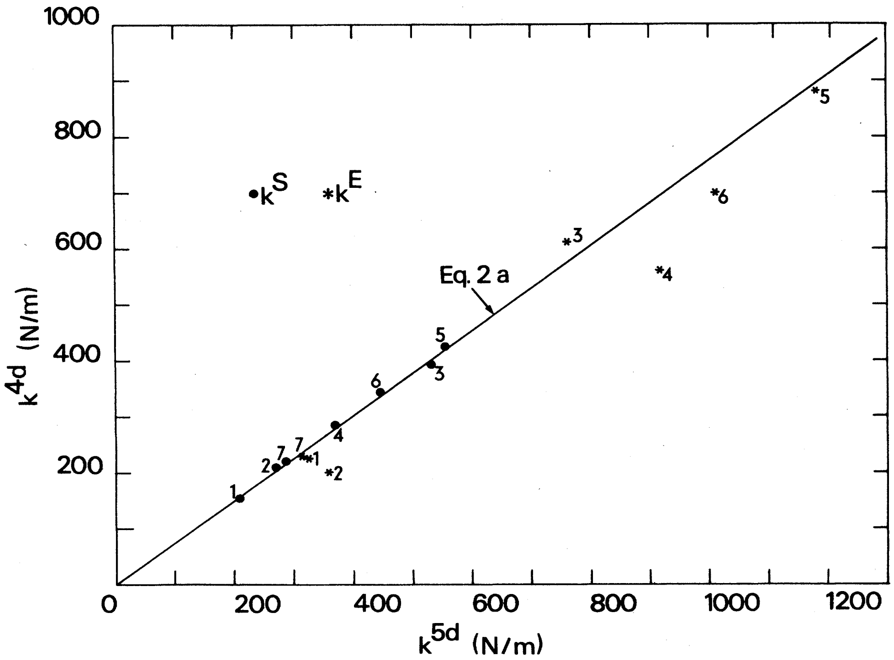

FIG. 1. The entropy-related force constants k^S for the $4d$ and $5d$ metals show pronounced homology. For the elastic-limit force constant k^E ($=k^{\text{elas}}$) there is less regularity. The numbers in the graph represent the following pairs of elements: (1) Zr,Hf, (2) Nb,Ta, (3) Mo,W, (4) Tc,Re, (5) Ru,Os, (6) Rh,Ir, (7) Pd,Pt. The relation $(k^S)^{4d}=0.76(k^S)^{5d}$, given in Eq. (2a), is shown as a straight line.

as one proceeds along the d series. The group-IIIB elements have been left out here because of the special properties of the lanthanides. The noble metals, with filled d shells, will also break the trends studied in this paper.

For comparison, we take the measured standard entropies ${}^0S=S(298\text{ K})$ and get the ratios $({}^0S)^{4d}/({}^0S)^{5d}=0.89\pm0.01$ for the seven pairs of metals considered here, while $({}^0S)^{3d}/({}^0S)^{4d}=0.87\pm0.08$. These ratios are only partly related to the results (1a) and (2a). In particular, the leading terms in the vibrational entropy of a Debye model with the Debye temperature Θ are[5] $S=3R[\frac{4}{3}+\ln(T/\Theta)+\frac{1}{40}(\Theta/T)^2+\ldots]$. As we move from $3d$ to $4d$ or from $4d$ to $5d$, the Debye temperature changes both because the atomic mass increases by approximately a factor of 2 and because of the force-constant changes discussed here. The electronic entropy is not very significant in this context.

Theoretically one has $\Theta^C=\Theta^{\text{elas}}$, which would make (1b) equal to (1c) and (2b) equal to (2c). We also note that our Θ^S refers to room temperature and hence to a slightly larger atomic volume than do our low-temperature values Θ^C and Θ^{elas}.

V. HOMOLOGY OF PHONON SPECTRA

The homology of k^S, and the somewhat less pronounced homology of k^C, k^{elas}, and k^B, raises the question whether the entire phonon spectrum, with the exception of its elastic limit, shows a homology between $4d$ and $5d$ transition metals. Neutron scattering data for the phonon frequencies $\omega(\mathbf{q})$ seem to be available only for the pairs Zr,Hf, Nb,Ta, Mo,W, and Pd,Pt. The absence of detailed homology for some pairs of elements is evident in Fig. 2, which shows $\omega(\mathbf{q})$ in the [100] direction, with ω^{5d} scaled by $[(k^S)^{4d}/(k^S)^{5d}]^{1/2}=0.87$ [cf. Eq. (2a)] and by $(M^{5d}/M^{4d})^{1/2}$ so that the dispersion curves for a given pair of elements would coincide in the case of detailed homology. Note in Fig. 2 how the transverse and longitudinal branches of the $4d$ element bracket those of the $5d$ element so that the averaged $\omega(\mathbf{q})$ shows better homology than does a single branch of $\omega(\mathbf{q})$.

A knowledge of the vibrational heat capacity $C(T)$ allows,[59] at least in principle, the evaluation of several moments $\omega(n)$ or Debye temperatures $\Theta(n)$, in addition to the cases $n=-3$ and $n=0$ considered above. For instance, $C(T)$ approaches the classical value $3R$ at high temperatures as $C(T)/3R=1-\frac{1}{20}[\theta(2)/T]^2$. However, there are several advantages to get $\Theta(0)$ from the entropy rather than getting $\Theta(2)$ from $C(T)$. A direct fit to $C(T)/3R$ at high temperatures leads to a very uncertain $\Theta(2)$ and anharmonic effects do not enter as simply as in the vibrational entropy. One therefore has to evaluate a temperature dependent $\Theta^C(T)$ at intermediate temperatures, plot is versus $1/T^2$, and extrapolate the plotted curve to $1/T^2=0$. Much the same information can, in our case, be obtained indirectly from theoretical calculations of phonon spectra. From such work, the moments $\omega(n)$ have been calculated[60] for Nb, Ta, Mo, W, Pd, and Pt. Although the absolute magnitude of $\omega(n)$ may not be very accurate, the results indicate that $\omega(0)$ and $\omega(2)$ typically differ by less than 2%.

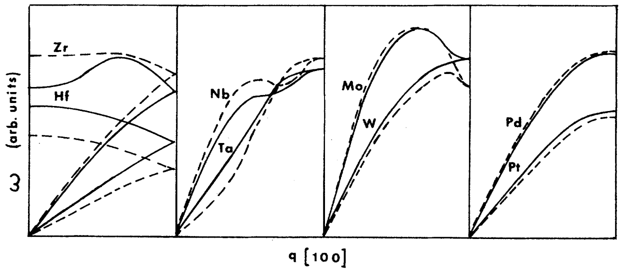

FIG. 2. The phonon dispersion curves $\omega(\mathbf{q})$ for wave vector $\mathbf{q}$ in the [100] direction, from the zone center to the boundary of the first Brillouin zone, based on neutron scattering data for Zr, (Ref. 51), Hf (Ref. 52), Nb, (Ref. 53), Ta, (Ref. 54), Mo (Ref. 55), W (Ref. 56), Pd (Ref. 57), and Pt (Ref. 58). The frequencies have been scaled (see text) so that they would coincide if they show the same homology as implied by our force constant k^S, Eq. (2a). The transverse and longitudinal branches of the $4d$ elements are dashed and those of the $5d$ elements are solid curves. Arbitrary units.

VI. DISCUSSION

Much theoretical work has been devoted to the bulk modulus and other elastic properties of the transition metals, e.g., a simple approach by Ducastelle,[61] the pioneering calculation by Moruzzi *et al.*[2] and recent work by Moruzzi *et al.*[62] To illustrate further the current accuracy, we quote results from Lu *et al.*[63] who calculated the atomic volume Ω and the bulk modulus in an *ab initio* local-density-functional scheme. They used two approximations for the exchange-correlation potential, the Hedin-Lundqvist (HL) and the $X\alpha$ ($\alpha=\frac{2}{3}$) forms. The differences between the experimental and the calculated values for hcp Ti and Zr are for the atomic volume 2% (Ti,$X\alpha$), 8% (Ti,HL), −1% (Zr,$X\alpha$), and 6% (Zr,HL) and for the bulk modulus −1% (Ti,$X\alpha$), −21% (Ti,HL), 11% (Zr,$X\alpha$), and −4% (Zr,HL). An *ab initio* calculation by Pictet[64] of the single-crystal elastic constants c_{ij} further testifies to the theoretical difficulties with varying crystal structures.

Since k^S depends on the logarithmic average of all phonon frequencies, k^{elas} is to some extent weighted into k^S. To get an idea of this effect, we assume that the Debye-like part of the phonon dispersion curves corresponds to $\frac{1}{8}$ of all phonon modes, with a force constant k^{elas}. The remaining modes are described by an effective force constant k^e. The logarithmic averaging yields $k^S=(k^e)^{7/8}(k^{\text{elas}})^{1/8}$. Then, from Table II, $(k^e)^{3d}/(k^e)^{4d}=0.87\pm0.18$ and $(k^e)^{4d}/(k^e)^{5d}=0.77\pm0.03$. These ratios are almost the same as those for k^S and the estimate does not crucially depend on the number $\frac{1}{8}$ chosen above.

Considering the difficulties mentioned above to account theoretically for the elastic constants c_{ij}, and the fact that a calculation of the large-wave-vector part of the phonon dispersion curves is more demanding than for c_{ij}, it seems likely that there is no simple theoretical explanation for the almost-constant k^S ratios.

Semiempirical methods have been very powerful in some related cases. For instance, there is a simple but accurate equation of state[3] for transition metals, which contains the bulk modulus, the cohesive energy, and the

Wigner-Seitz radius as parameters. In our search of simple empirical relations we note that the dimension of k^S is force per length, or energy per area. It would be natural to interpret the area as $\Omega^{2/3}$. Since Ω^{4d}/Ω^{5d} is almost a constant, one is led to look for some characteristic energy E with a constant ratio E^{4d}/E^{5d}. The width of the d band, E_d, might be a possible candidate. We estimate E_d from Papaconstantopoulos[65] and form the quantity $E'=E_d/\Omega^{2/3}$. Then, $(E')^{4d}/(E')^{5d}=0.79\pm0.07$. As an alternative, we form $(E'')^{4d}/(E'')^{5d}$, where $E''=E_{\text{coh}}/\Omega^{2/3}$, and get 0.84 ± 0.09. The cohesive energy E_{coh} is taken from Brewer.[66] Neither of the two ratios shows the remarkable constancy of k^S or Ω ratios.

VII. COMMENTS ON APPLICATIONS

Several of the metals covered in this work, and their alloys, have poorly known properties and there is a need for guidelines in estimations and assessments of experimental data. We have found that the quantity k^S varies less than, e.g., k^{elas}, k^C, and k^B. This is of practical importance because many properties should be better described by parameters related to k^S than to elastic constants. For instance, the temperature-dependent part of the Gibbs energy at high temperatures is dominated by the high-frequency phonons. Other examples are diffusion and dislocation glide which involve atomic displacements not well described by the elastic-limit phonon modes. Still, one often uses models which, for the lack of better information, contain a Debye temperature or a similar parameter taken from the elastic limit of the phonon dispersion curves. In such cases, we suggest that the parameter of interest is estimated from k^S, because this may not only be a more relevant quantity but it is often more accurately estimated.

As an example, consider Nb-Mo alloys, which form bcc solid solutions for all concentrations c. $\Theta^C(T\rightarrow0\text{ K})$ varies considerably, from $\Theta^C=277$ K (Nb) to $\Theta^C=470$ K (Mo); see Table I. The dependence of $\Theta^C(T\rightarrow0\text{ K})$ on the alloy composition is known from heat-capacity data[67] and can be inferred from data on c_{ij}.[68] Since the atomic masses of Nb and Mo are almost equal, variations in Θ^C are due to force-constant changes. But Θ^S taken at room temperature varies much less than $\Theta^C(T\rightarrow0\text{ K})$, from 282 K (Nb) to 380 K (Mo). If the low-temperature data for Θ^C are used to estimate the vibrational entropy of $\text{Nb}_{0.5}\text{Mo}_{0.5}$ at room temperature, the error may be as large as the entire ideal entropy of mixing, $-R[c\ln c+(1-c)\ln(1-c)]=R\ln2$. An interpolation between Θ^S of Nb and Mo is likely to give a much better estimate of $S_{\text{vib}}(300\text{ K})$ than a calculation based on the measured Θ^C or Θ^{elas} of the alloy. In this context we remark that we have not found any experimental data that would allow a direct test of our homology relations for transition metal alloys.

As another example, consider the separation of the total entropy of a magnetic solid into its magnetic (S_{mag}), electronic and vibrational contributions in the paramagnetic state. If there are heat-capacity data covering the region of the magnetic order-disorder transformation one can draw a base line in the $C_P(T)$ curve and estimate the paramagnetic S_{mag}. In fcc Fe, on the other hand, there are neutron scattering measurements of the phonon dispersion curves, which enables a separation of S_{mag}.[69] In many other cases, e.g., Mn, S_{mag} has to be inferred by more indirect methods. Weiss and Tauer[70] performed such an analysis based on what they considered to be reasonable Debye temperatures of the Mn phases. A similar procedure could be adopted, but now on a much firmer ground, using the parameter Θ^S and its trends shown by the present study and an account of the nonmagnetic thermodynamics as described, e.g., by Grimvall *et al.*[44] Some work in this direction has been made.[71]

As a final example of applications, we mention our recent work on Tc,[38] where Eq. (2a), combined with information from low-temperature heat-capacity data, was used to estimate the high-temperature properties.

VIII. CONCLUSIONS

We have introduced generalized force constants k. Among them, k^S which is related to the vibrational entropy is of particular interest. It is accurately obtainable from thermodynamic data and includes all parts of the phonon branches, i.e., not only the elastic limit of the dispersion curves. This force constant varies less than that derived from the elastic limit and its ratios k^{4d}/k^{5d} for 4d and 5d transition metal groups in the Periodic Table are almost constant. The corresponding ratios k^{3d}/k^{4d} show a larger variation. An accurate *ab initio* account of the force constants seems to lie beyond the level of current calculations of the electronic structure of transition metals. The regularity of the force constants is of interest as a challenge to the theoretical understanding of the binding forces and lattice dynamics in transition metals. It is also of practical value in the estimation or assessment of experimental data.

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[1] K. A. Gschneidner, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 275.

[2] V. L. Moruzzi, A. R. Williams, and J. F. Janak, Phys. Rev. B **15**, 2854 (1977); V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, Oxford, 1978).

[3] J. H. Rose, J. R. Smith, F. Guinea, and J. Ferrante, Phys. Rev.

B **29**, 2963 (1984); P. Vinet, J. R. Smith, J. Ferrante, and J. H. Rose, Phys. Rev. B **35**, 1945 (1987).

[4] G. Grimvall and J. Rosén, Int. J. Thermophy. **4**, 139 (1983); G. Grimvall and M. Thiessen, in *Institute of Physics Conference Proceedings Series* (IOP, Bristol, 1986), Vol. 75, p. 61.

[5] J. Rosén and G. Grimvall, Phys. Rev. B **27**, 7199 (1983).

[6] G. Grimvall, Phys. Scr. **14**, 63 (1976); *The Electron-Phonon Interaction in Metals* (North-Holland, Amsterdam, 1981).

[7] Scientific Group Thermodata Europe (SGTE), Pure Transition Metal Data, complied by A. T. Dinsdale, National Physical Lab., U.K. (1988).

[8] As an example, let the magnetic heat capacity in Fe at low temperatures T be $0.047T^{3/2}$ mJ/mol K. That would increase our Θ^S by $<1\%$. Cf. G. Grimvall, Phys. Scr. **13**, 59 (1976).

[9] N. E. Phillips, Crit. Rev. Solid State Sci. **2**, 467 (1971).

[10] J. K. D. Verma and M. D. Aggarwal, J. Appl. Phys. **46**, 2841 (1975).

[11] R. F. S. Hearmon, in *Landolt-Börnstein: New Series,* edited by K.-H. Hellwege and A. M. Hellwege (Springer, Berlin, 1979 and 1984), Vol.s II/11 and III/18.

[12] P. D. Desai, Int. J. Thermophys. **8**, 781 (1987).

[13] M. Singh and S. Tolpadi, Indian J. Pure Appl. Phys. **21**, 140 (1983). They use c_{ij} from G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook* (MIT Press, Cambridge, 1971).

[14] P. D. Desai, Int. J. Thermophys. **7**, 213 (1986).

[15] G. K. White, R. B. Roberts, and E. Fawcett, J. Phys. F **16**, 449 (1986).

[16] P. D. Desai, J. Phys. Chem. Ref. Data **16**, 91 (1987).

[17] G. L. Guthrie, S. A. Friedberg, and J. E. Goldman, Phys. Rev. **139**, A1200 (1965).

[18] G. L. Booth, F. H. Hoare, and B. T. Murphy, Proc. Phys. Soc. London, Sect. B **68**, 830 (1955).

[19] G. R. Stewart, Rev. Sci. Instrum. **54**, 1 (1983).

[20] S. Shinozaki, A. Arrott, H. Sato, and J. E. Zimmerman, Bull. Am. Phys. Soc. **8**, 66 (1963).

[21] R. G. Elson, H. Grayson-Smith, and J. O. Wilhelm, Can. J. Res. Sect. A **18**, 83 (1940).

[22] L. D. Armstrong and H. Grayson-Smith, Can. J. Res. Sect. A **27**, 9 (1949).

[23] P. Franzosini, C. G. Losa, and K. Clusius, Z. Naturforsch. **19a**, 1348 (1964).

[24] K. Takemura, O. Shimomura, K. Hase, and T. Kikegawa, J. Phys. F **18**, 197 (1988).

[25] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **64**, 51 (1929).

[26] J. C. Slater, Phys. Rev. **57**, 744 (1940).

[27] F. Birch, Phys. Rev. **71**, 809 (1947).

[28] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 71 (1948).

[29] J. J. Gilvarry, J. Chem. Phys. **23**, 1925 (1955).

[30] D. J. Steinberg, J. Phys. Chem. Solids **43**, 1173 (1982).

[31] M. Rosen, Phys. Rev. **165**, 357 (1968).

[32] N. M. Wolcott, J. Chem. Phys. **31**, 536 (1959).

[33] P. D. Desai, Int. J. Thermophys. **8**, 763 (1987).

[34] A. Fernández Guillermet, High Temp.—High Pressures **19**, 119 (1987).

[35] E. S. Fisher and C. J. Renken, Phys. Rev. **135**, A482 (1964).

[36] A. Fernández Guillermet, Int. J. Thermophys. **6**, 367 (1985).

[37] R. J. Trainor and M. B. Brodsky, Phys. Rev. B **12**, 4867 (1975).

[38] A. Fernández Guillermet and G. Grimvall, J. Less-Common Met. **147**, 195 (1989).

[39] E. Walker, J. Ashkenazi, and M. Dacorogna, Phys. Rev. B **24**, 2254 (1981).

[40] K. Clusius and C. Gutiérrez Losa, Z. Naturforsch. **10a**, 545 (1955).

[41] N. M. Wolcott, Conference de Physique de Basses Temperature, Paris 1955, LT5 Conf. Proc., Suppl. Inst. Int. Froid, Annexe 1955-3, p. 286 (1955).

[42] D. W. Budworth, F. E. Hoare, and J. Preston, Proc. R. Soc. London, Ser. A **257**, 250 (1960).

[43] G. T. Furukawa, M. L. Reilly, and J. S. Gallagher, J. Phys. Chem. Ref. Data **3**, 163 (1974).

[44] G. Grimvall, M. Thiessen, and A. Fernández Guillermet, Phys. Rev. B **36**, 7816 (1987).

[45] D. R. Smith and P. H. Keesom, Phys. Rev. B **1**, 188 (1970).

[46] M. L. Shepard and J. F. Smith, J. Appl. Phys. **36**, 1447 (1965).

[47] W. Köster and H. Franz, Metall. Rev. **6**, 1 (1961).

[48] C. P. Kempter, Phys. Status Solidi **8**, 161 (1965).

[49] R. E. MacFarlane, J. A. Rayne, and C. K. Jones, Phys. Lett. **20**, 234 (1966).

[50] H.-G. Purwins, H. Hieber, and R. Labusch, Phys. Status Solidi **11**, K63 (1965).

[51] C. Stassis, J. Zarestky, D. Arch, O. D. McMasters, and B. N. Harmon, Phys. Rev. B **18**, 2632 (1978).

[52] C. Stassis, D. Arch, O. D. McMasters, and B. N. Harmon, Phys. Rev. B **24**, 730 (1981).

[53] Y. Nakagawa and A. D. B. Woods, Phys. Rev. Lett. **11**, 271 (1963).

[54] A. D. B. Woods, Phys. Rev. **136**, A781 (1964).

[55] B. M. Powell, P. Martel, and A. D. B. Woods, Can. J. Phys. **55**, 1601 (1977).

[56] A. Larose and B. N. Brockhouse, Can. J. Phys. **54**, 1819 (1976).

[57] A. P. Miiller and B. N. Brockhouse, Can. J. Phys. **49**, 704 (1971).

[58] D. H. Dutton, B. N. Brockhouse, and A. P. Miiller, Can. J. Phys. **50**, 3069 (1972).

[59] T. H. K. Barron, W. T. Berg, and J. A. Morrison, Phys. Soc. London Ser. A **242**, 478 (1957).

[60] H. R. Schober and P. H. Dederichs, in *Landolt-Börnstein: New Series,* edited by K.-H. Hellwege and J. L. Olsen (Springer, Berlin, 1981), Vol. III/13.

[61] F. Ducastelle, J. Phys. (Paris) **31**, 1055 (1970).

[62] V. L. Moruzzi, J. F. Janak, and K. Schwarz, Phys. Rev. B **37**, 790 (1988).

[63] Z-W. Lu, D. Singh, and H. Krakauer, Phys. Rev. B **36**, 7335 (1987). Comparison is made with our adopted B. Lu *et al.* seem to misquote B of Zr.

[64] O. Pictet, Ph.D. thesis, Université de Genève, 1986.

[65] D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

[66] L. Brewer, Lawrence Berkeley Laboratory Report No. LBL-3720, 1977 (unpublished). $E_{\rm coh}$ is defined as the sublimation energy at 0 K.

[67] G. K. White, J. G. Collins, J. A. Birch, T. F. Smith, and T. R. Finlayson *Transition Metals,* Institute of Physics Conference Series No. 39 edited by M. J. G. Lee, J. M. Perz, and E. Fawcett (IOP, Bristol, 1978), p. 420.

[68] P. Bujard, R. Sanjines, E. Walker, J. Ashkenazi, and M. Peter, J. Phys. F **11**, 775 (1981).

[69] G. Grimvall, Phys. Rev. B **40** (to be published).

[70] R. J. Weiss and K. J. Tauer, J. Phys. Chem. Solids **4**, 135 (1958).

[71] A. Fernández Guillermet and Huang Weiming (unpublished).