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Correlation and Prediction of Parameters Related to Vibrational Properties of Compounds[1]

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The vibrational contribution to the Gibbs energy G of solids is often expressed in a simple algebraic form in terms of the absolute temperature. This paper discusses how parameters entering such an expression for G are expected on theoretical grounds to show certain regularities and, hence, may be estimated for a certain compound if they are known for chemically related compounds. The regularities of the parameters are exemplified by the sp^3-bonded solids Si, Ge, α-Sn, and III–V semiconducting compounds.

KEY WORDS: cohesive properties; Gibbs energy; high temperatures; lattice vibrations; III–V semiconductors.

1. INTRODUCTION

In thermodynamic modeling the Gibbs energy G of a stoichiometric phase or compound is often expressed as [1, 2]

$$G = a_0 + bT + cT\ln(T) + dT^{-1} + eT^2 + fT^3 \qquad (1)$$

T is the absolute temperature, and $a_0, b, \ldots$, are fitted parameters. In the Calphad [3] type of assessment, the fitting aims at a representation that is consistent with all available thermodynamic information on the system.

This paper deals with how theoretical results restrict the algebraic form of G and lead to quantities that have a smooth and regular behavior and hence allow for interpolations and extrapolations. Many of the ideas presented here have been applied previously to alkali halides [4], actinide

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dioxides [5], alkali earth halides [6], simple metals [7], transition metals [8–10], transition metal carbides and nitrides [11–13], and diborides [14]. The reader is referred to that work for details. Here we focus on the implications for the form of G in Eq. (1), with an application to the sp^3-bonded solids Si, Ge, α-Sn, AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, and InSb.

2. REPRESENTATION OF THE VIBRATIONAL ENTROPY

2.1. Series Expansions

It is preferable to discuss the entropy S, rather than G. From Eq. (1),

$$S = -b - c - c\ln(T) + dT^{-2} - 2eT - 3fT^2 \tag{2}$$

The high-temperature expansion of S for harmonic phonons is [15]

$$\begin{aligned} S = 3Nk_B\{&1 + \ln[k_B T/h\omega(0)] + \tfrac{1}{24}[h\omega(2)/k_B T]^2 \\ &- \tfrac{1}{960}[h\omega(4)/k_B T]^4 + \cdots\} \end{aligned} \tag{3}$$

N is the number of atoms, k_B is Boltzmann's constant, and $\omega(n)$ are moments of the phonon density of states $F(\omega)$,

$$\omega(n) = \left[\int F(\omega)\omega^n\,d\omega \Big/ \int F(\omega)\right]^{1/n} \tag{4}$$

when $n \neq 0$ and with $\ln[\omega(0)]$ being the average of $\ln \omega$. Often it is convenient to work with Debye temperatures $\theta(n)$, defined such that a Debye spectrum with cutoff energy $k_B\theta(n)$ would yield a frequency moment $\omega(n)$. Hence,

$$k_B\theta(n) = \left[\frac{n+3}{3}\right]^{1/n} h\omega(n) \tag{5}$$

when $n \neq 0$ and $k_B\theta(0) = \exp(1/3)\,h\omega(0)$. The expansion (3) becomes

$$S = 3Nk_B\{4/3 + \ln[T/\theta(0)] + \tfrac{1}{40}[\theta(2)/T]^2 - \tfrac{1}{2240}[\theta(4)/T]^4 + \ldots\} \tag{6}$$

2.2. Debye Temperatures from Experimental Data

From heat capacity data $C_p(T)$ one obtains a "heat capacity Debye temperature" θ_C through

$$C_p(T) = C_D(T/\theta_C) \tag{7}$$

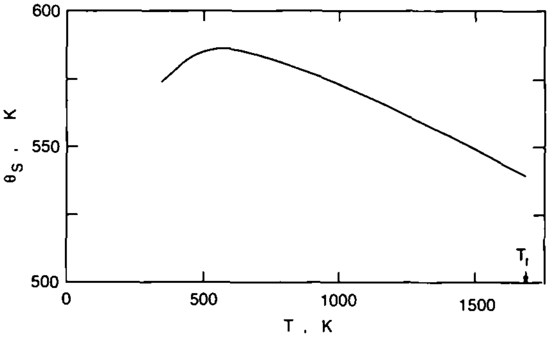

Fig. 1. The entropy Debye temperature $\theta_S(T)$ defined by Eq. (8) and evaluated for silicon from recommended [21] entropy data.

where C_D is the Debye-model expression for the heat capacity. Similarly, vibrational entropy data $S_p(T)$ yield an "entropy Debye temperature" θ_S through

$$S_p(T) = S_D(T/\theta_S) \tag{8}$$

where S_D is the Debye-model expression for the entropy. Since the true phonon spectrum is not harmonic and not of the Debye form, the solutions θ_C and θ_S to Eqs. (7) and (8) will be temperature dependent (cf. Fig. 1). At high temperatures, when anharmonic effects make $C_p > 3Nk_B$, Eq. (7) has no solution. Hence, $\theta_C(T)$ has an unphysical behavior at high temperatures, which may be present even if one considers C_V instead of C_p (cf. Ref. 9).

Contrary to $\theta_C(T)$, the entropy Debye temperature $\theta_S(T)$ is well behaved at all temperatures (Fig. 1). According to Eq. (6), $\theta_S(T)$ for *harmonic* vibrations asymptotically approaches $\exp(1/3)\,\hbar\omega(0)/k_B$. In real systems, $\theta_S(T)$ usually decreases with T at high temperatures, due to anharmonic softening of the phonon frequencies. Reference 5 discusses how one may use the fact that anharmonic effects are small for temperatures $T < \theta_S$ and construct an asymptotic $\theta(0)$ that can be considered as the harmonic part and how one also obtains $\theta(2)$. $\theta(0)$ is central in our discussion below. A more easily accessible quantity, and a good approximation to $\theta(0)$, is θ_S evauated at $T \approx \theta_S$. Around this temperature $\theta_S(T)$ varies slowly with T and θ_S can be determined from tabulated entropy values.

3. TWO THEOREMS ON Θ_S

3.1. Anharmonic Phonon Frequency Shifts

It has been shown [16, 17] that the entropy is correctly obtained to low order in perturbation theory if the anharmonically shifted phonon frequencies are used in the harmonic expression for the vibrational entropy. Hence, $\omega(0)$ in Eq. (3) should be evaluated from the temperature-dependent frequency spectrum, e.g., as it may be determined from inelastic neutron scattering data. Further, in low-order perturbation theory the anharmonic shift in the phonon frequencies is linear in T for $T \gtrsim \theta_S$. Therefore, let $\theta(0) = \theta_0(0)[1 + AT]$. Comparing Eqs. (2) and (6), with $AT \ll 1$, gives

$$b = 3Nk_B \ln[\theta_0(0)] - Nk_B \tag{9}$$

$$c = -3Nk_B \tag{10}$$

$$d = \tfrac{3}{40} Nk_B[\theta(2)]^2 \tag{11}$$

$$e = \tfrac{3}{2} Nk_B A \tag{12}$$

As the melting temperature T_f is approached, higher-order anharmonic effects may become important and give $\theta_S(T)$ a nonlinear T dependence. Such effects contribute to a T^2 term and still higher powers of T in Eq. (2).

3.2. Separation of the Influence of Atomic Masses

Another important theoretical result refers to how the atomic masses affect G. One can show [4] that in the logarithmically averaged phonon frequency $\omega(0)$, and hence also in $\theta(0)$, the atomic masses enter only as a multiplicative factor. We can write

$$k_B \theta(0) = h \sqrt{k_B / M_e} \tag{13}$$

The effective mass M_e is the logarithmically averaged atomic mass in the compound, and k_S has the dimension of a force constant. It follows that

$$b = 3Nk_B \{\ln(h/k_B) - \tfrac{1}{2} \ln(M_e) - \tfrac{1}{2} \ln(k_S)\} - Nk_B \tag{14}$$

where k_S refers to the force constant at $T \approx \theta(0)$.

In the quantum mechanical description above, the Gibbs energy G depends only on the atomic masses through a term $(3Nk_B T/2)\ln(M_e)$. This is consistent with a classical statistical mechanics description, which is valid at high temperatures. Then the atomic masses enter the partition function only through the kinetic energy. It follows that G depends on the masses only through a term $\ln M_e$, irrespective of anharmonic effects.

4. APPLICATION TO sp^3-BONDED SOLIDS

4.1. Temperature Dependence of θ_S

In Fig. 1 we show $\theta_S(T)$ for silicon, evaluated through Eq. (8) and using recommended entropy data [21]. A series expansion of θ_S/T in terms of $S(T)/k_B$ [5] facilitates a quick calculation of $\theta_S(T)$ for $T \gtrsim \theta_S/3$. The shape of $\theta_S(T)$ in Fig. 1 is characteristic of many solids and has been discussed elsewhere [5, 7, 9, 13]. However, the high-temperature part of $\theta_S(T)$ in Fig. 1 is unusually linear in T, and the total decrease in $\theta_S(T)$ from $T \approx \theta_S$ to the melting temperature T_f is smaller than found for, e.g., metallic elements [7, 9] and actinide dioxides [5]. We conclude that anharmonic shifts in the phonon frequencies of Si are, on the average, small and well described by low-order perturbation theory. This fact also causes the maximum in the plot of $\theta_S(T)$ versus T for Si to be at a higher $T/\theta_S(T)$ than is normally observed. We remark that $\theta_S(T)$ may in some cases (e.g.,

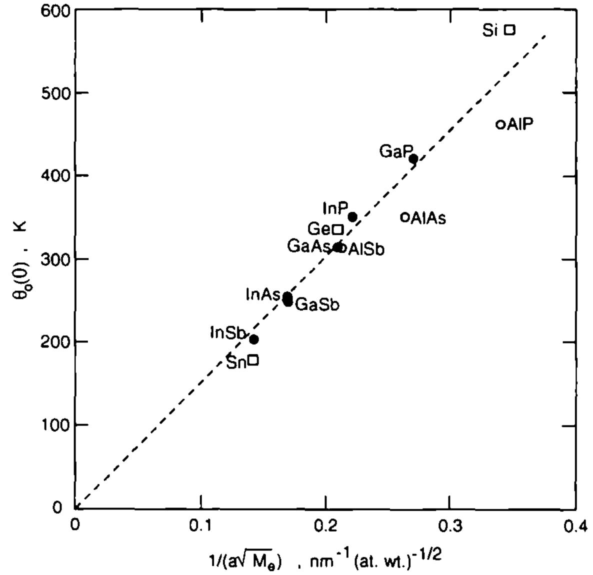

Fig. 2. The entropy Debye temperature θ_S, represented here by the value $\theta_0(0)$ evaluated when $T \approx \theta_S$, varies approximately linearly with $1/[a(M_e)^{1/2}]$, where a is the lattice parameter and M_e is an effective atomic mass equal to the logarithmically averaged mass in the compound. All compounds shown have the sphalerite (ZnS) structure. The dashed line is a guide for the eye.

metals with hexagonal crystal structure [7]) decrease continuously for all T, with a plateau around $T \approx \theta_S$, where normally a broad maximum is found.

Solids with similar chemical bonding have similar plots of $\theta_S(T)/\theta_0$ versus T/T_f [5, 7, 9]. The parameter A may then be estimated if $S(T)$ is known for related solids; compare discussions of Tc [18], CrC [19], and Cr_3C [20].

4.2. Regularities for $\theta_0(0)$

We shall approximate $\theta_0(0)$ by the value of θ_S at $T \approx \theta_S$, where $\theta_S(T)$ varies slowly (cf. Fig. 1 and the discussion above). Equation (13) shows that hypothetical solids of the same crystal structure, and with identical bonding but different atomic masses would have $\theta(0)$, and hence also θ_0, that differ only through the multiplicative factor $1/\sqrt{M_c}$. If these solids have the same shapes of the potentials $\Phi(\mathbf{r}/s)$ giving the interatomic forces for a separation vector $\mathbf{r}$, but with different scaling lengths s, one can show [4] that all $\theta(n)$ vary with s as $1/s$. Further, the latice parameter a for such a (cubic) system would be proportional to s. These considerations lead us to consider plots of $\theta(0)$ versus $1/(a\sqrt{M_c})$. Figure 2 shows such a plot for sp^3-bonded solids, with $\theta_0(0)$ from recommended entropy data [2, 21] and a from Ref. 22. The solids in Fig. 2 all have the sphalerite (ZnS) structure and are chemically related. Hence we expect their bonding to be very similar. A manifestation of these facts is the good correlation shown in Fig. 2.

5. PARAMETERS ENTERING THE GIBBS ENERGY REPRESENTATION

We now discuss the implications for the representation in Eq. (1) of the Gibbs energy. The crucial parameter in the temperature dependence of G is $b = 3Nk_B \ln[\theta_0(0)] - Nk_B$. Suppose that we know θ_S for a class of chemically related compounds of the same crystal structure. Then $\theta_0(0)$ for a compound for which no entropy data are available could be estimated through interpolation or extrapolation in a plot such as Fig. 2. An example could be ternary compounds of the III–V family, e.g., $Ga_xIn_{1-x}As$, and relying on the regularity in Fig. 2.

When the compared compounds do not all have the same crystal structure, the length parameter a that was used in Fig. 2 becomes ambiguous. We have found [11, 12, 14] that very regular plots are often obtained if we consider a quantity E_S with the dimension of energy

$$E_S = k_S \Omega_a^{2/3} \tag{15}$$

Ω_a is the average volume per atom in the compound, and k_S is directly related to the vibrational entropy. E_S was found to be remarkably constant in a group of 20 alkali earth halides [6], in spite of varying crystal structures. However, it is no general rule that E_S is independent of the crystal structures. For instance, ZnS in the sphalerite structure (i.e., the structure of the compounds in Fig. 2) has $\theta_S = 370$ K at $T \approx \theta_S$, while ZnS in the wurtzite structure has $\theta_S = 296$ K, although their Ω_a differ by only about 1 % and the structures have the same coodination number of 4.

E_S is a suitable quantity when one studies compounds that are related but have varying strength of the bonding. The reader is referred to graphs of E_S versus the average number of valence electrons per atom, for transition metal carbides and nitrides [11, 12] and diborides [14].

Next we turn to the parameter c in Eq. (1) for G. If c is left as a free parameter instead of taking $c = 3Nk_B$, one must compensate for this in the other parameters. Then they lose their regular behavior discussed above (cf. a discussion for actinide dioxides [5]).

The parameter d is related to the average squared phonon frequency, expressed by a Debye temperature $\theta(2)$. Lacking other information, one may take $\theta(2) \approx \theta_0(0)$; see a study of the various phases of Mn [23]. A plot of $\theta_C(T)$ versus $1/T^2$, with $\theta_C(T)$ from Eq. (7), may also be used to obtain $\theta(2)$ [5].

The parameter e, describing anharmonic effects, may be estimated from a comparison with $\theta_S(T)/\theta_0(0)$ versus T/T_f for related compounds, as mentioned in Section 4. It does not depend on the atomic masses.

The parameter a_0 cannot be determined without information on the enthalpy at some reference temperature. Its determination lies outside the scope of the present paper, but we remark that the enthalpy of formation ΔH in a group of related compounds shows a strong correlation with E_S [11, 12, 14]. Further, one often checks the consistency of the Gibbs energy G in Eq. (1) by performing phase diagram calculations and comparing the predictions with experiments [24–26].

6. CONCLUSIONS

The vibrational part of the Gibbs energy $G(T)$ may be represented by a simple algebraic expression in T. We have discussed how theoretical results from lattice dynamics have implications for the parameters entering such an expression for G and how that can be used to establish regularities among them. It follows that the parameters entering G of a certain compound may be estimated if they are known for chemically related compounds. The regularities are exemplified by the sp^3-bonded solids Si, Ge, α-Sn, and III–V semiconductor compounds.

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