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Vibrational Entropy of Polyatomic Solids: Metal Carbides, Metal Borides, and Alkali Halides

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It is shown that in the high temperature vibrational entropy of polyatomic solids, the influence of the atomic masses is described by an effective mass $M_e = M_1^{c_1} M_2^{c_2} \ldots M_j^{c_j}$, where c_i is the concentration of mass M_i. This mass effect explains almost all of the differences between TiC, ZrC, and HfC in the recommended entropy data of Hultgren et al. (1973). Analogous results are found for VC, NbC, and TaC and for TiB_2, ZrB_2, and HfB_2. Mass differences also explain a major part of the measured entropy differences between alkali halides AB, with A = Li, Na, or K and B = F, Cl, Br, or I. Finally, we discuss different methods, including one used in the JANAF Thermochemical Tables, to estimate standard entropies from data on chemically related compounds.

KEY WORDS: alkali halides; entropy; lattice vibrations; metal borides; metal carbides.

1. INTRODUCTION

In monatomic solids, the phonon frequencies $\omega(\mathbf{q},\lambda)$ are all proportional to $M^{-1/2}$, where M is the atomic mass. In polyatomic solids, there is in general no such simple scaling of $\omega(\mathbf{q},\lambda)$. However, in the average $\langle \ln \omega(\mathbf{q},\lambda) \rangle$ over all phonons $(\mathbf{q},\lambda)$, the mass dependence is $\ln(M_e^{-1/2})$ with an effective mass $M_e = M_1^{c_1} M_2^{c_2} \ldots M_j^{c_j}$. The quantities M_i and c_i are the masses and concentrations of the atom of kind i in the unit cell. This particular average yields the high temperature vibrational entropy S. In this paper we shall use experimental data on $S(T)$ in order to discuss lattice vibrations in some polyatomic solids, when the mass dependence is separated out. We analyze metal carbides MeC, where Me is Ti, Zr, Hf, V, Nb,

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or Ta; metal diborides MeB_2, where Me is Ti, Zr, or Hf; and alkali halides AB, where A is Li, Na, or K and B is F, Cl, Br, or I.

In Section 2 we recapitulate some results for the entropy of lattice vibrations. The mass dependence of $\langle \ln \omega \rangle$ is derived in Section 3. Section 4 discusses the application to real crystals, and in Section 5 we discuss the validity of a method used, e.g., in the JANAF Thermochemical Tables [1] to estimate $S(T)$ of a solid when no direct experimental data are available.

2. THE VIBRATIONAL ENTROPY

Consider a crystal with r atoms per unit cell and N unit cells. The $3rN$ phonon frequencies are $\omega(\mathbf{q}, \lambda)$, where $\mathbf{q}$ is the wave vector and λ is a mode index (longitudinal or transverse modes, acoustic or optical branches). $F(\omega)$ is the phonon density of states, normalized to 3 per atom. The vibrational entropy S, and its high temperature expansion, is

$$\begin{aligned} S &= Nrk_B \int_0^{\omega_{\max}} \left[(1+n)\ln(1+n) - n\ln(n) \right] F(\omega)\, d\omega \\ &= Nrk_B \int_0^{\omega_{\max}} \left[1 + \ln(k_B T/\hbar\omega) + \frac{1}{24}(\hbar\omega/k_B T)^2 \right. \\ &\qquad \left. - \frac{1}{960}(\hbar\omega/k_B T)^4 + \cdots \right] F(\omega)\, d\omega \end{aligned} \tag{1}$$

Here, n is the Bose–Einstein function, $n = [\exp(\hbar\omega/k_B T) - 1]^{-1}$. We define Debye temperatures $\theta(n)$ for $n > -3$ such that, for a given n, the nth moment calculated from $F(\omega)$ is the same as the moment calculated in a Debye model with frequency cut-off $\omega_D(n) = k_B \theta(n)/\hbar$, i.e.,

$$\int_0^{\omega_D} \omega^n \omega^2\, d\omega \Big/ \int_0^{\omega_D} \omega^2\, d\omega = \int_0^{\omega_{\max}} \omega^n F(\omega)\, d\omega \Big/ \int_0^{\omega_{\max}} F(\omega)\, d\omega \tag{2}$$

When $n = 0$, ω^n is replaced by $\ln \omega$.

The high temperature expansion of S in Eq. (1) can be written

$$S = 3rNk_B \left[\frac{4}{3} + \ln(T/\theta(0)) + \frac{1}{40}\left(\frac{\theta(2)}{T}\right)^2 - \frac{1}{2240}\left(\frac{\theta(4)}{T}\right)^4 + \cdots \right] \tag{3}$$

Suppose that the entropy of a system with an arbitrary density of states

$F(\omega)$ is put equal to the entropy calculated from a Debye model, with energy cut-off $k_B\theta_S$. At each temperature, this defines an "entropy Debye temperature" $\theta_S(T)$. The high temperature expansion of $\theta_S(T)$ is [2]

$$\theta_S(T) = \theta(0)\left(1 + \sum_{n=1}^{\infty} a_n T^{-2n}\right) \tag{4}$$

with

$$a_1 = \frac{1}{40}\left[\theta^2(0) - \theta^2(2)\right] \tag{5}$$

$$a_2 = \frac{1}{2240}\left[\theta^4(4) - \theta^4(0)\right] + \frac{a_1}{2}\left[a_1 + \frac{1}{10}\theta^2(0)\right] \tag{6}$$

In a strict Debye model, $\theta(n) = \theta_D$ for all n, and $\theta_S(T) = \theta_D$ is independent of T.

If $\theta_S(T)$ is derived from the measured vibrational entropy of a real crystal, $\theta_S(T)$ is temperature dependent for two different reasons. When $T \lesssim \theta_S/2$, $\theta_S(T)$ varies with T because $F(\omega)$ is not a Debye spectrum. The corresponding high temperature dependence is given in Eq. (4). When $T \gtrsim \theta_S$, $\theta_S(T)$ varies with T (usually a decrease) because the anharmonicity of the lattice vibrations (which includes thermal expansion) becomes important. When $\theta_S/2 \lesssim T \lesssim \theta_S$, $\theta_S(T)$ varies slowly with T. We are interested in the ratios of θ_S for different compounds, and choose to consider $\theta_S' \equiv \theta_S(T)$ evaluated (iteratively) at $T = \theta_S'$. θ' is very close (error $\lesssim 1\%$) to $\theta(0)$ taken at the crystal volume $V(T = \theta')$. We take $\theta(0) = \theta'$ and thus get a very good estimate of the average $\langle \ln \omega(\mathbf{q}, \lambda)\rangle$ over all modes $(\mathbf{q}, \lambda)$.

If the uncertainty in the experimental entropy is δS (at a temperature $T' \gtrsim \theta_S$), it follows from Eq. (3) that the related uncertainty $\Delta\theta$ in θ_S is given by

$$|\Delta\theta|/\theta_S \simeq (4/3)(|\delta S|/S) \tag{7}$$

3. THE ATOMIC MASS DEPENDENCE OF $\langle \ln \omega(\mathbf{q}, \lambda)\rangle$

The phonon frequencies $\omega(\mathbf{q}, \lambda)$ are obtained from the eigenvalues of the quation

$$\det(\mathbf{D} - \omega^2\mathbf{I}) = 0 \tag{8}$$

where $\mathbf{D}(\mathbf{q})$ is the $3r \times 3r$ dynamical matrix and $\mathbf{I}$ is the unit matrix. The $3r$

roots ω_λ^2 of Eq. (8) obey the relation

$$\prod_{\lambda=1}^{3r} \omega_\lambda^2 = \det \mathbf{D}(\mathbf{q}) \tag{9}$$

The dynamical matrix can be written [3]

$$\mathbf{D} = \mathbf{M}^{-1/2}\mathbf{D}_0\mathbf{M}^{-1/2} \tag{10}$$

The matrix $\mathbf{D}_0(\mathbf{q})$ only contains the interatomic forces and no atomic masses. The mass tensor $M^{1/2}$ is diagonal with elements $(M_1^{1/2}, M_1^{1/2}, M_1^{1/2}, \ldots, M_r^{1/2}, M_r^{1/2}, M_r^{1/2})$, i.e., each atomic mass appears three times for every such atom in the unit cell. $M^{-1/2}$ has diagonal elements $M_1^{-1/2}$, etc. Since

$$\det \mathbf{D} = \det\left(\mathbf{M}^{-1/2}\mathbf{D}_0\mathbf{M}^{-1/2}\right) = \left[\det\left(\mathbf{M}^{-1/2}\right)\right]^2 \det \mathbf{D}_0 \tag{11}$$

one has

$$\begin{aligned} \langle \ln \omega(\mathbf{q},\lambda) \rangle &= \frac{1}{6rN} \sum_{\mathbf{q}} \ln(\det \mathbf{D}) \\ &= \frac{1}{6rN} \sum_{q} \ln\left[\det \mathbf{D}_0(\mathbf{q})\right] + \ln\left(\prod_{i=1}^{r} M_i^{-1/2r} \right) \end{aligned} \tag{12}$$

We write the last term, with an effective mass, as $\ln(M_e^{-1/2})$. Then

$$M_e = M_1^{c_1} M_2^{c_2} \ldots M_j^{c_j} \tag{13}$$

where c_i is the concentration of mass i $(0 < c_i < 1)$. Hence, the quantity

$$\alpha = M_e^{1/2}\theta(0) \tag{14}$$

which can be obtained from the high temperature vibrational entropy, gives a measure of the effective interatomic forces but is independent of the atomic masses.

4. APPLICATION TO REAL CRYSTALS

4.1. Metal Carbides

The entropy Debye temperature $\theta_S(T)$ is calculated for TiC, ZrC, HfC, VC, NbC, and TaC from the recommended (experimental) entropy data of Hultgren et al. [4]. We evaluate $\theta_S(T)$ over a wide range of

Table I. Vibrational Parameters of Metal Carbides

Compound	θ_S [a] (K)	$\frac{\theta_S}{\theta_S(\text{MeC})}$ [a]	$\frac{\alpha}{\alpha(\text{MeC})}$ [b]
TiC	805	1	1
ZrC	650	0.81	0.95
HfC	581	0.72	1.00
VC	745	1	1
NbC	634	0.85	0.99
TaC	551	0.74	1.02

[a] $\theta_S(T)$ evaluated at $T \sim \theta_S$.
[b] MeC is TiC for group IV B and VC for group V B metal carbides.

temperatures to ensure that there are no irregularities in $\theta_S(T)$ which would cast doubts on the selected $S(T)$ (cf. a discussion on this point by Grimvall and Rosén [5]). The compounds are assumed to have the ideal stoichiometric composition MeC. Deviation from this condition has only a small influence on the effective mass M_e but adds a term S_c to the entropy. We assume (lacking more detailed information) that S_c is independent of T from low T up to $T = \theta_S$. Then our $\theta_S(T)$, which is calculated from $S(T) - S(0)$, is unaffected by S_c.

The carbides, and the borides in Section 4.2, are metallic (cf. searches for superconductivity [6]). The conduction electrons contribute S_{el} to the total entropy. We neglect that term for the following reason. Its low temperature part appears not to be very well known. The smallness of $C_p - 3Nk_B$[4] at high T ($\sim$2000 K), a quantity which is expected to contain a large anharmonic contribution in addition to C_{el}, suggests that $S_{el}/S \lesssim 0.02$ at $T \sim \theta(0)$. Since S_{el} presumably is of the same order of magnitude within each of the three groups of compounds treated here, an inclusion of S_{el} would alter the normalized numbers in the last column of Tables I and II by $\lesssim 1\%$. In other metallic compounds, S_{el} may be nonnegligible.

Table I gives θ_S when $T \simeq \theta_S$, the normalized θ_S/θ_S(TiC) or θ_S/θ_S(VC) and the likewise normalized parameters α/α(TiC) or α/α(VC). The latter correspond to what θ_S/θ_S(TiC) or θ_S/θ_S(VC) would be if the influence of the atomic mass is suppressed. It is quite remarkable how similar the interatomic forces (as expressed by α) are for the three carbides of the same metal group in the periodic table.

4.2. Metal Diborides

Table II gives the results for TiB_2, ZrB_2, and HfB_2, calculated as was done for the metal carbides, from data by Hultgren et al. [4]. Again, the

Table II. Vibrational Parameters of Metal Diborides

Compound	$\theta_S{}^a$ (K)	$\frac{\theta_S}{\theta_S(\mathrm{TiB_2})}$	$\frac{\alpha}{\alpha(\mathrm{TiB_2})}$
TiB_2	974	1	1
ZrB_2	867	0.89	0.99
HfB_2	738	0.76	0.94

[a] $\theta_S(T)$ evaluated at $T \sim \theta_S$.

variation in $\theta_S(T)$, or the vibrational entropy, is almost entirely due to the difference in atomic masses.

4.3. Alkali Halides

Table III gives our results for all the alkali halides with NaCl structure, for which entropy data are given in the JANAF Thermochemical Tables [1]. The values for LiBr and LiI in [1] are estimates based on a method which we discuss in Section 5. Although the atomic mass difference in most cases is the dominating reason why $\theta_S/\theta_S(\mathrm{NaCl}) \neq 1$, the effective interatomic forces are not as invariant as was found for the metal carbides and borides.

Table III. Vibrational Parameters of Alkali Halides

Compound	$\theta_S{}^a$ (K)	$\frac{\theta_S}{\theta_S(\mathrm{NaCl})}$	$\frac{\alpha}{\alpha(\mathrm{NaCl})}$	$\frac{a\alpha}{a(\mathrm{NaCl})\alpha(\mathrm{NaCl})}$
LiF	589	2.16	1.37	0.98
NaF	419	1.53	1.31	1.07
KF	306	1.12	1.10	1.04
LiCl	355	1.30	0.96	0.88
NaCl	273	1	1	1
KCl	222	0.81	0.93	1.04
LiBr	(262)[b]	(0.96)[b]	(0.87)[b]	(0.85)[b]
NaBr	204	0.77	0.92	0.97
KBr	170	0.62	0.87	1.02
LiI	(208)[b]	(0.76)[b]	(0.78)[b]	(0.84)[b]
NaI	159	0.58	0.80	0.92
KI	139	0.51	0.80	1.00

[a] $\theta_S(T)$ evaluated at $T \sim \theta_S$.

[b] Estimated values. See Section 5.

When the interatomic forces scale with the lattice parameter a, as would be the case for the interaction related to the Madelung type contribution, θ_S varies as $1/a$. In the last column of Table III we allow for this "size effect" and give $\alpha/\alpha(\text{NaCl})$ multiplied by $a/a(\text{NaCl})$. It is remarkable how well the "mass effect" (which we can handle exactly) plus the "size effect" (which is only an approximate correction, but empirically justified here) can account for the difference in θ_S among the alkali halides. A corresponding lattice parameter correction for the carbides and borides is not meaningful. They have a different kind of chemical binding, with forces that do not scale simply with a.

5. A METHOD TO ESTIMATE THE ENTROPY

Due to lack of low temperature heat capacity data for LiBr and LiI, S (298 K) for these compounds was estimated in the JANAF Thermochemical Tables [1] from

$$S\,(\text{LiBr}) = S\,(\text{NaBr}) - S\,(\text{NaCl}) + S\,(\text{LiCl}) \tag{15}$$

and

$$S\,(\text{LiI}) = S\,(\text{NaI}) - S\,(\text{NaCl}) + S\,(\text{LiCl}) \tag{16}$$

We shall now discuss the theoretical justification for such a prescription.

First, suppose that for all four compounds in (15) or (16), the interatomic forces contribute equally to $\theta(0)$, i.e., $\alpha = M_e^{1/2}\theta(0)$ is the same. Then it is easily seen that (15) and (16) hold in the high temperature limit at which the first two terms in Eq. (3) suffice to give S. At lower temperatures, corrections to (15) and (16) will arise even if all the solids obey a strict Debye model, i.e., even if $\theta(n) = \theta_D$ for all n.

As a numerical example, we assume that $\theta(n) = \theta_D = \alpha M_e^{-1/2}$, with appropriate effective masses M_e, for all four compounds in [15]. We then calculate $S(T)$ within a Debye model for these four alkali halides. At $T = \theta_D(\text{NaCl})$, the left-hand side of (15) differs from the calculated right-hand side by less than 1%. With decreasing T, the difference gets larger and is about 7% when $T = \frac{1}{2}\theta_D(\text{NaCl})$. If we allow for the size effect and take $\alpha \propto a$, relation (15) is still valid in the high temperature limit provided that $\beta = a(\text{LiBr})/[a(\text{NaBr})a(\text{LiCl})/a(\text{NaCl})]$ is unity. Crystallographic data give $\beta = 1.01$. For relation (16), the corresponding value is $\beta = 1.03$.

In view of the discussion above, the use of relations (15) and (16) seems justified, but this is partly fortuitous. For some combinations of alkali halides, the conditions on the temperature and on the lattice parameter ratios are not fulfilled. This brings us to one of the main points of this paper, namely, a prescription to estimate unknown entropies. There is no *a priori* reason for the quantity $\alpha = M_e^{1/2}\theta(0)$ to be a constant, even among chemically related compounds. However, Tables I and II show empirically that α is approximately constant for the investigated carbides and borides. Therefore, one can have some confidence in $\theta(0)$ calculated for groups of other chemically related transition metal carbides and borides, even if $\theta(0)$ is based on α for only one compound within such a group. In the case of alkali haldies, even the lattice parameter corrected α is not as invariant as for the carbides and borides. The entropy has been measured for 10 of the 12 compounds in Table III. A reasonable empirically based procedure would then be to assign entropy values to the two remaining compounds (LiBr and LiI) such that the numbers in the last column of Table III show a regular behavior. The entries for LiF and LiCl are significantly lower than those for NaF, KF, NaCl, and KCl. The estimates in the JANAF tables are consistent with such a trend also for the bromides and iodides. Kelley and King [7] have also estimated standard entropies $S(298)$ of LiBr and LiI. Their data lead to values of 0.97 (LiBr) and 1.01 (LiI) in the last column of Table III, which is somewhat high if the trend mentioned above is to be obeyed.

6. CONCLUSIONS

We have shown that in the vibrational entropy S of polyatomic crystals at high temperatures, the influence of atomic masses can be separated from the dependence of S on the interatomic forces. This was done for recommended entropy data of some metal carbides, metal diborides, and alkali halides. The mass difference accounts for almost all of the difference in entropy among the chemically related carbides or borides. The mass effect is the main reason also for differences in S among the alkali halides, and a simple ion size effect accounts for most of the remaining differences. This kind of analysis may be used to give a plausibility check on available entropy data, or provide an estimate of $S(T)$ when no direct measurements are available for a particular system.

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