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Correlation and Prediction of Thermodynamic Data for Oxide and Silicate Minerals[1]

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Often one needs to estimate heat capacities and related properties such as the entropy for a particular material through interpolation, extrapolation, or comparison with data for related materials. A scheme is discussed to perform such estimates, focusing on the vibrational entropy. At intermediate and high temperatures, the entropy depends only on the logarithmic average over the phonon frequencies. This average can be factorized, so that the atomic masses separate from the interatomic force constants. Thus, one can account for the mass effect in the vibrational entropy and get a remaining quantity which depends only on the force constants, i.e., on the electronic structure, and shows a strong regularity when chemically similar materials are compared. In the framework of these ideas, estimates based on an additivity rule for the entropy of a complex system in terms of the entropies of the constituents, and also relations between the vibrational entropy and sound velocities, are discussed. Oxide and silicate minerals are used as examples.

KEY WORDS: Debye temperature; entropy; lattice vibrations; oxide minerals; phonons; silicate minerals; thermodynamic data.

1. INTRODUCTION

The major contribution to the thermodynamic functions of solids comes from the lattice vibrations. The phonon spectra for most elements and many simple compounds are known from experiments and can often be calculated theoretically, with phonon frequencies predicted to better than 5–10%. Contrasting with this, the phonon spectra are usually not known

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from experiments for complex solids, such as minerals of geophysical interest. Instead, simple empirical rules and semiempirical modeling based on, e.g., measured elastic properties, have been used [1]. We first briefly review the theoretical background of a systematic approach to the vibrational spectrum as it is manifested in the entropy. This approach has been applied by our group to transition metal carbides, nitrides [2, 3], borides [4], binary semiconductors [5], and binary ionic solids [6–9]. The reader is referred to these works and Refs. 10–12 for further aspects of the theory. This paper extends such studies to more complex solids, choosing oxide and silicate minerals as an illustration.

2. REPRESENTATION OF A PHONON SPECTRUM

Let a phonon spectrum be described by its density of states $F(\omega)$, normalized to 3 per atom, where ω is a phonon frequency. From $F(\omega)$ we form frequency moments $\omega(n)$ defined as

$$[\omega(n)]^n = \tfrac{1}{3} \int_0^{\omega_{\max}} \omega^n F(\omega)\, d\omega \tag{1}$$

when $n > -3$ and $n \neq 0$. The limiting behavior for $n = 0$ yields

$$\ln[\omega(0)] = \tfrac{1}{3} \int_0^{\omega_{\max}} \ln(\omega)\, F(\omega)\, d\omega \tag{2}$$

The same information that is contained in $\omega(n)$ can also be expressed as "Debye temperatures," $\theta_D(n)$. We define $\theta_D(n)$ such that a Debye spectrum with cutoff frequency $\omega_{\max} = k_B \theta_D(n)/\hbar$ has the corresponding frequency moment $\omega(n)$, i.e.,

$$k_B \theta_D(n) = \left(\frac{n+3}{3}\right)^{1/n} \hbar\omega(n) \tag{3}$$

for $n \neq 0$, where k_B and $\hbar$ are Boltzmann's and Planck's constants, respectively. When $n = 0$, we get $k_B \theta_D(0) = \exp(1/3)\, \hbar\omega(0)$. Hence $\theta_D(n) = \theta_D$ for all n in a spectrum with the Debye model form, characterized by θ_D (i.e., $\omega_{\max} = k_B \theta_D/\hbar$). A real spectrum is not of the Debye form, and the quantities $\theta_D(n)$ describing $F(\omega)$ vary with n.

Some important physical quantities depend on only *one* moment $\omega(n)$, i.e., on only one $\theta_D(n)$. For example, the low-temperature heat capacity and entropy correspond to $n \rightarrow -3$, the high-temperature heat capacity to $n = -2$, and the high-temperature entropy (see below) to $n = 0$. The elastic constants uniquely give the low-frequency limit of the phonon frequencies.

Therefore, elastic data can also be used to calculate $\theta_D(n)$ for $n \to -3$. The representation of the spectrum $F(\omega)$ by $\theta_D(n)$ is motivated by the connection to the often used Debye model, for example, through the publication of Debye temperatures. It must be stressed that since our $\theta_D(n)$ for different n are not equal, we can deal with any form of the phonon density of states $F(\omega)$.

3. THE VIBRATIONAL ENTROPY

The vibrational entropy of harmonic lattice vibrations has the high-temperature expansion

$$S(T) = Nk_B \int_0^{\omega_{\max}} [1 + \ln(k_B T/\hbar\omega) + (1/24)(\hbar\omega/k_B T)^2 + \cdots] F(\omega)\, d\omega \tag{4}$$

N is the number of atoms in the solid. This expression depends on all the $3N$ vibrational frequencies that enter $F(\omega)$. However, at high T the leading terms in Eq. (4) are

$$S(T) \approx 3Nk_B\{1 + \ln[k_B T/\hbar\omega(0)]\} = 3Nk_B\{4/3 + \ln[T/\theta_D(0)]\} \tag{5}$$

Hence, $S(T)$ at high T is essentially determined by a single parameter, $\omega(0)$ or $\theta_D(0)$.

Let the vibrational entropy in a strict Debye model, with a Debye temperature θ_S, be $S_D(T; \theta_S)$. Further, let the experimentally determined vibrational entropy of a solid be $S_{\exp}(T)$. The relation

$$S_D(T; \theta_S) = S_{\exp}(T) \tag{6}$$

yields a solution $\theta_S(T)$ for each T. This is analogous to the more frequently used procedure to get a Debye temperature $\theta_C(T)$ for the heat capacity C by equating the Debye model expression $C_D(T; \theta_D)$ with an experimental result $C_{\exp}(T)$. From the discussion above, it follows that $\theta_S(T \to 0) = \theta_D(-3)$. Of more importance for our subsequent work is the high-temperature relation $\theta_S(T) \approx \theta_D(0)$; cf. Eq. (5).

4. $\theta_S(T)$ OF $MgAl_2O_4$

As an illustration, we calculate $\theta_S(T)$ for $MgAl_2O_4$ from the experimental entropy data recommended in the JANAF tables [13]. The result is given in Fig. 1. That figure also shows the Debye temperature

$\theta_{\mathrm{elast}}(T)=\theta_D(-3)$ calculated from measured elastic constants in the temperature range 300 to 1000 K [1]. At $T=0$, $\theta_S=\theta_{\mathrm{elast}}$. At temperatures up to appoximately 300 K, $\theta_S(T)$ shows a strong temperature dependence. This reflects the fact that the true phonon spectrum of $MgAl_2O_4$ is not of the strict Debye model shape. $\theta_S(T)$ at these temperatures results from a weighting of the frequencies in $F(\omega)$ which cannot be reduced to a single $\omega(n)$. At high temperatures, however, $\theta_S(T)$ only depends on $\omega(0)$. The decrease in $\theta_S(T)$ with temperature in that region is due to anharmonic effects in the lattice vibrations. One can show that to low order in quantum mechanical perturbation theory the vibrational entropy is correctly accounted for if the anharmonically shifted phonon frquencies are inserted in Eq. (4) that is derived for harmonic vibrations. Therefore, $\theta_S(T)$ has a well-defined physical meaning also at high temperatures. This is in contrast to a Debye temperature $\theta_C(T)$ derived from the heat capacity $C_{\mathrm{exp}}(T)$, that is also shown in Fig. 1. When the actual heat capacity exceeds the Dulong-Petit limit of $3k_B$ per atom, the equation $C_D(T;\theta_C)=C_{\mathrm{exp}}(T)$ has no physical solution. Not even the heat capacity C_V at constant volume has the limiting value $3k_B$/atom at high T. Hence $\theta_C(T)$ is not a physically well defined quantity at high T even if it is fitted to C_V. The temperature dependence of θ_{elast} in Fig. 1 is, of course, also due to anharmonic effects.

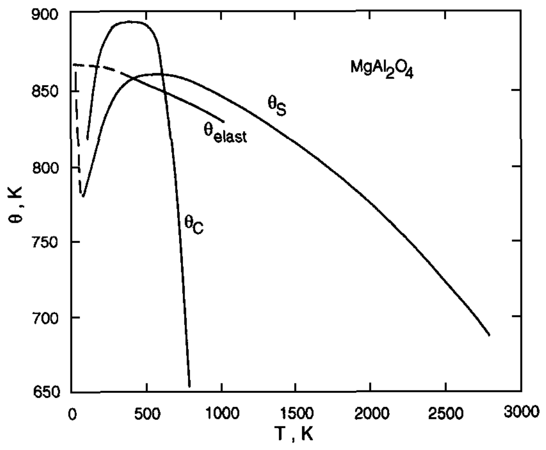

Fig. 1. The entropy Debye temperature $\theta_S(T)$ of $MgAl_2O_4$ calculated from Eq. (6) and recommended experimental entropy data [13]. θ_{elast} is the conventional Debye temperature based on sound velocities [1], and $\theta_C(T)$ is the Debye temperature calculated from experimental heat capacities [13].

5. THE ATOMIC-MASS DEPENDENCE OF $\theta_D(0)$

Phonon frequencies depend on the interatomic forces and on the atomic masses. In the elastic limit (i.e., small ω), all frequencies vary as $\rho^{-1/2}$, where ρ is the mass density in the solid. A separation of atomic masses and interatomic forces occurs also in the averaged frequency $\omega(0)$. We may formally write

$$k_B\theta_D(0) = \hbar\omega(0)\exp(1/3) = \hbar\sqrt{k_S/M_{\log}} \tag{7}$$

Here k_S (subscript S because it can be derived from entropy data) has the physical dimension of a force constant, and is a complicated average for all the interatomic forces in the solid. $M_{\log}$ is the logarithmic average of the atomic masses.

The quantity k_S, or equivalently the quantity $M_{\log}[\theta_D(0)]^2$, depends on the electronic structure of a solid, but not on the atomic masses. The lattice parameters and the average volume per atom Ω_a in the solid (total volume V divided by the number of atoms N) also depends only on the electronic structure. Hence, any combination $k_S(\Omega_a)^p$ is independent of the atomic masses. It can be expected to vary in a regular way when compared for chemically similar compounds. If $p = 2/3$, the quantity $k_S(\Omega_a)^p$ has the dimension of energy. We therefore define the entropy-related energy $E_S = k_S(\Omega_a)^{2/3}$. E_S often shows a trend similar to that of other bonding-related quantities of the same dimension, e.g., the cohesive energy E_{coh} or the quantity $k_B T_m$ where T_m is the melting temperature [2–4]. For alkali halides [6], alkali oxides [7], and other simple ionic solids [8], E_S is remarkably constant, even when solids with different crystal structures are compared.

6. AN ADDITIVITY RULE FOR THE ENTROPY

We now consider the vibrational entropy S_{AB} of a complex solid with a chemical composition that can be summarized as AB, where A and B are themselves more or less complex solids. If S_A and S_B are known, but not S_{AB}, it may be tempting to estimate S_{AB} from an additivity rule

$$S_{AB} = S_A + S_B \tag{8}$$

This scheme was tried by Latimer [10, 14] when A and B are elements. Holland [15] applied it to minerals, and others, including Blander and Stover [16], Richet et al. [17], and Navrotsky [18], have followed a similar path. We shall now discuss the additivity rule within the framework of lattice dynamics outlined above.

From Eqs. (5) and (7) we see that the additivity rule [Eq. (8)] gives a correct account of the atomic masses in the vibrational entropy at high temperatures. This conclusion is not affected by anharmonic effects. Therefore (at high T) a violation of Eq. (8) is caused only by electronic-structure effects. Some of the bonds within the units A and B are almost unchanged when these units are combined in the solid AB, and do not contribute to a violation of Eq. (8). To get a simple physical description of deviations from the additivity rule, we express the difference between an actually measured S_{AB} and the sum of the measured S_{A} and S_{B} as a relative shift $\Delta\theta_{\mathrm{S}}$ in the entropy Debye temperature θ_{S} for the compound AB. Since $\Delta\theta_{\mathrm{S}}/\theta_{\mathrm{S}}$ is small, we have, from Eq. (5) and at high temperatures,

$$\frac{\Delta\theta_{\mathrm{S}}}{\theta_{\mathrm{S}}} \approx -\frac{S_{\mathrm{AB}} - S_{\mathrm{A}} - S_{\mathrm{B}}}{3Nk_{\mathrm{B}}} \tag{9}$$

where N is the total number of atoms in the solid AB. Table I gives $\Delta\theta_{S}/\theta_{\mathrm{S}}$ for some oxide and silicate minerals. Data are from Saxena et al. [19]. SiO_2 exists in many forms. For comparison, Table I therefore refers to quartz α-SiO_2, as well as to cristobalite, SiO_2(crist.).

The strengths of the interatomic forces tend to increase with decreasing volume per atom, as has been frequently noted by our group (cf. E_{S} above) and others; see references in Ref. 1. Holland [15] suggested an empirical correction to the additivity rule, invoking molar volumes. In Fig. 2 we therefore correlate $\Delta\theta_{\mathrm{S}}/\theta_{\mathrm{S}}$ with the average volume par atom to see how

Table I. Relative Shift in Entropy Debye Temperature

Reaction	$\Delta\theta_{\mathrm{S}}/\theta_{\mathrm{S}}$ (%)
$MgO + Al_2O_3 \rightarrow MgAl_2O_4$(spinel)	−2.6
$MgO + SiO_2(\alpha) \rightarrow MgSiO_3$(orthoenstatite)	2.8
$2MgO + SiO_2(\alpha) \rightarrow Mg_2SiO_4$(forsterite)	0.7
$Al_2O_3 + SiO_2(\alpha) \rightarrow Al_2SiO_5$(andalusite)	1.3
$Al_2O_3 + SiO_2(\alpha) \rightarrow Al_2SiO_5$(kyanite)	5.8
$2MgO + 2Al_2O_3 + 5SiO_2(\alpha) \rightarrow Mg_2Al_4Si_5O_{18}$(corderite)	−7.3
$3MgO + Al_2O_3 + 3SiO_2(\alpha) \rightarrow Mg_3Al_2Si_3O_{12}$(pyrope)	−2.2
$MgO + SiO_2$(crist.) $\rightarrow MgSiO_3$(orthoenstatite)	5.5
$2MgO + SiO_2$(crist.) $\rightarrow Mg_2SiO_4$(forsterite)	2.7
$Al_2O_3 + SiO_2$(crist.) $\rightarrow Al_2SiO_5$(andalusite)	3.0
$Al_2O_3 + SiO_2$(crist.) $\rightarrow Al_2SiO_5$(kyanite)	7.5
$2MgO + 2Al_2O_3 + 5SiO_2$(crist.) $\rightarrow Mg_2Al_4Si_5O_{18}$(corderite)	−4.9
$3MgO + Al_2O_3 + 3SiO_2$(crist.) $\rightarrow Mg_3Al_2Si_3O_{12}$(pyrope)	−0.2

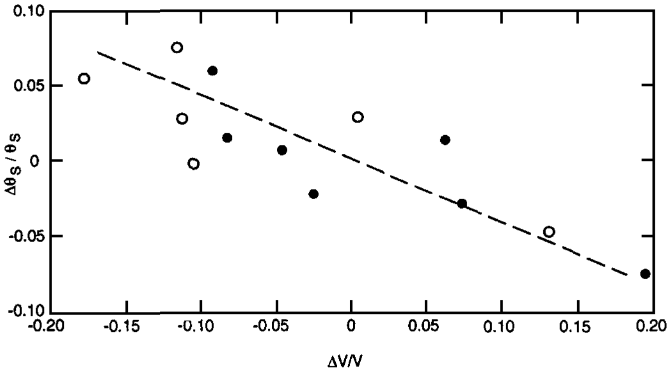

Fig. 2. The violation of the entropy additivity rule, Eq. (8), expressed as a corresponding relative shift in the entropy Debye temperature, $\Delta\theta_S/\theta_S$, plotted versus an analogous difference in the average volume per atom $\Delta V/V$, for the systems in Table I. Filled circles refer to calculations based on α-SiO_2, and open circles to SiO_2(cristalobalite).

well an additivity rule holds. We define a relative volume shift $\Delta V/V = (V_{AB} - V_A - V_B)/V_{AB}$, with molar volumes V from Saxena et al. [19]. The filled circles refer to combinations with α-SiO_2, and open circles refer to combinations with cristobalite which has lower θ_S by 4.5% and higher V by 12% than α-SiO_2. The dashed line in Fig. 2 is only a guide for the eye. We conclude from Table I that the additivity rule often predicts the Debye temperature θ_S with an error $<5\%$, which is better than can be expected even from an ambitious theoretical calculation in the absence of thermodynamic data. We also see from Fig. 2 that θ_S does correlate with changes in the volume per atom (often related to a change in coordination numbers for the atoms), but corrections based on such a trend are not very accurately predicted in these cases. However, invoking such a correction in our case would predict θ_S to better than 3%.

7. RELATION BETWEEN $\theta_D(0)$ AND SOUND VELOCITIES

The Debye temperature $\theta_D(-3)$ appearing in the low-temperature limit of the heat capacity is proportional to an average sound velocity v_a, where $3/v_a^3 = 2/v_s^3 + 1/v_p^3$. The low velocity v_s associated with the transverse (shear) mode dominates v_a. As a conseqence $\theta_D(-3)$ is strongly correlated to the shear modulus G but depends weakly on the bulk modulus B [20]. The logarithmic average $\omega(0)$ of interest here gives a considerable weight also to longitudinal phonon modes, which are strongly affected by B. Further, B may be rather easily obtained in an *ab initio* theoretical calculation, while G is more difficult to calculate and has more uncertainty. Therefore *ab initio* calculations extended to finite temperatures have often invoked an empirical relation between B and a Debye temperature that is then used to describe temperature effects [21, 22]. Such a procedure could be motivated by the empirical fact [23] that $\theta_D(0)$ for many metals of cubic structure is slightly better correlated to B than to G. However, there have also been doubts that this scaling of $\theta_D(0)$ is generally useful. In Fig. 3 we look at such relations for some minerals. The elastic-limit Debye temperature θ_{elast} as tabulated by Anderson [1] is plotted (filled circles) versus our $\theta_S \approx \theta_D(0)$ derived from the measured entropy at temperatures $T \approx \theta_S/2$. This plot essentially shows a correlation of θ_S to G. The open circles are based on a θ_{elast} with v_a replaced by a scaled average

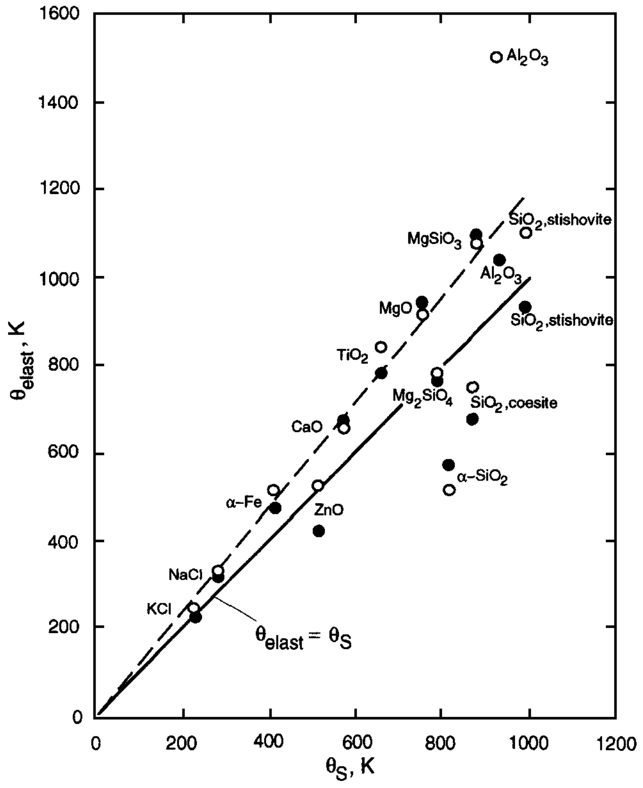

Fig. 3. The conventional Debye temperature θ_{elast} based on the sound velocities (filled circles) plotted versus the entropy Debye temperature θ_S, and the analogous plot with θ_{elast} based only on a rescaled longitudinal sound velocity (open circles). The dashed line is just a guide for the eye.

longitudinal sound velocity αv_{p}, with v_{p} also taken from Anderson [1] and $\alpha = 2/3$ being an empirical scaling factor that brings many of the θ_{elast} based on v_{a} and αv_{p}, respectively, to approximately coincide in Fig. 3. This procedure gives a θ_{elast} with a considerable weight of B. We see that an empirical relation between $\theta_{\mathrm{D}}(0)$ and the average longitudinal sound velocity, through a Debye-type relation, is as good as a direct correlation of $\theta_{\mathrm{D}}(0)$ to $\theta_{\mathrm{elast}} = \theta_{\mathrm{D}}(-3)$. The solid line in Fig. 2 is the relation $\theta_{\mathrm{elast}} = \theta_{\mathrm{S}}$, i.e., the correlation if θ_{S} were identical to the conventional low-temperature Debye temperature, θ_{elast}. The dashed line is just a guide for the eye, showing that θ_{elast} is often somewhat larger than θ_{S}. It is also clear from Fig. 3 that some solids strongly violate a close correlation between θ_{S} and θ_{elast}; cf. a discussion by Anderson [1].

8. CONCLUSIONS

We have studied the additivity rule $S_{\mathrm{AB}} = S_{\mathrm{A}} + S_{\mathrm{B}}$ for the vibrational entropy S of a compound AB, expressed in its components A and B, with data for oxide and silicate minerals. At high temperatures ($T > \theta_{\mathrm{S}}$), the rule is equivalent to the prediction of an entropy Debye temperature θ_{S} with an error $< 5\%$. If we also allow for a correction based on the average volume per atom, the error in θ_{S} is typically $< 3\%$. A major reason for the applicability of the additivity rule is that it correctly accounts for the effect of atomic masses on the vibrational spectra, thus leaving only electron structure effects as a reason for $S_{\mathrm{AB}} \neq S_{\mathrm{A}} + S_{\mathrm{B}}$ at high temperatures. The theoretical framework of the present analysis, using effective Debye temperatures to represent certain frequency moments of the phonon spectrum, allows a straightforward comparison with conventional Debye temperatures referring to the heat capacity at low and intermediate temperatures.

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