

## Evaluation of the subambient temperature dependence of the heat capacity of crystalline and vitreous substances

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### Abstract

*To resolve transitional entropies and thermophysical contributions to the heat capacity extending over relatively large ranges of temperature, we have developed two rather specialized methods for the evaluation of the (vibrational) lattice heat capacity valid to a high degree of accuracy compared to the typical extant procedures. The earlier developed method is designated the "Volume Priority Method," and it takes into account the relative predominance of volume (rather than mass) over the "chemical thermodynamic region" below 300 K. It has been employed in recent years in the resolution of Schottky contributions arising from the splitting of the ground state by the crystalline electric fields of lanthanide salts with excellent results. The newer method is the "Komada/Westrum Phonon Density Distribution" method and although it has a generic resemblance to the well-known Debye approach it succeeds where Debye fails. It has been used for the resolution of magnetic and other transitions in such mineral systems as deerite and grunerite and enables the resolution even of minute electron delocalization phenomena. Finally, taking advantage of recent developments in the closely related Barber-Martin approach in the analysis of heat capacities, we extend the treatment to alkali silicates—both vitreous and crystalline. Meaningful values are provided for several fundamental physical parameters which correlated with other elastic and thermal properties by (in contrast to Debye theory) taking the dispersion and the resolution of acoustic and optic modes into account. Differences in the primitive volume between vitreous and crystal phases are noted and the extension of the Komada/Westrum treatment to vitreous phases enabled.*

### INTRODUCTION

Although the measured *total* heat capacities provide the requisite thermophysical data for thermodynamic applications by integration, in many instances the resolution of the *excess* contributions be they Schottky, magnetic, ferroelectric, order/disorder, or other is of major interest to the researcher. But the exact evaluation of the excess contribution depends on recognition of the "lattice" heat capacity and its resolution. Since the latter typically represents more than 90% of the measured heat capacity, its contribution must be evaluation accurately and precisely.

Two of the most commonly used approaches are those of Latimer [1,2] and of Debye [3], but neither is truly adequate. The former—used primarily for estimation of entropies of compounds in the absence of measurements—attributes an entropy contribution to each anion and represents that of the cation by a logarithmically couched function of the atomic mass. The misleading aspect of Latimer's approach became apparent after the study of transition-element chalcogenides by Grønvald and Westrum [4] and the depiction of the data in Figure 1. Apart from a surprising constancy of the entropies throughout the d-electron transition element series is the perpendicularity of the lanthanide family's dependence to the predicted logarithmic mass dependence. Here, where cationic masses and molar volumes are clearly disparate as a consequence of the "lanthanide contraction" it is evident that "volume priority" clearly overrides "mass priority" as has been demonstrated in our works on lanthanide sesquisulfides [5], sesquioxides, trihydroxides, halides, etc. despite Grimvall's [6] mathematical "defense" of Latimer's approach. Yes, mass needs to be factored into the argument at very low temperatures, for example, but over the chemical thermodynamic region, volume is clearly the variable to be reckoned with as shown in Figure 2.

We have developed our "volume priority" theory by a simple linear interpolation of heat capacity across—in the light lanthanides—lanthanum and gadolinium molar volumes and this calculation is repeated (isothermally) over the entire temperature range. It has been used effectively and accurately. The Debye heat-capacity function [3] was known by Debye himself to be a crude approximation on structureless continuums, without reference to geometry, simplified by assumption of constant acoustical wave velocity, but despite their failure they are widely used to represent aspects of the temperature morphology of heat-capacity curves. It did, however, trigger the independent analysis of Born and Von Kármán [8,9] on the lattice vibrational spectrum. Many others contributed to the solid-state vibrational theory, but inasmuch as we recognize a limited goal, the full details of lattice dynamics are rather more than we can afford to cope with, particularly in the characteristic absence of thermal expansion values on crystals of interest.

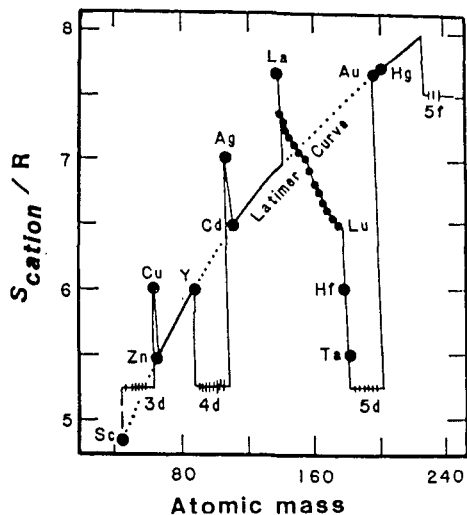


Fig. 1. Comparison of Grønvoold and Westrum's scheme [4] against the background of the Latimer scheme (o.....o). The Latimer-scheme contributions: (o), experimental values for the lanthanide cations [7]; (—) experimental values for the transition-elemental cations [4].

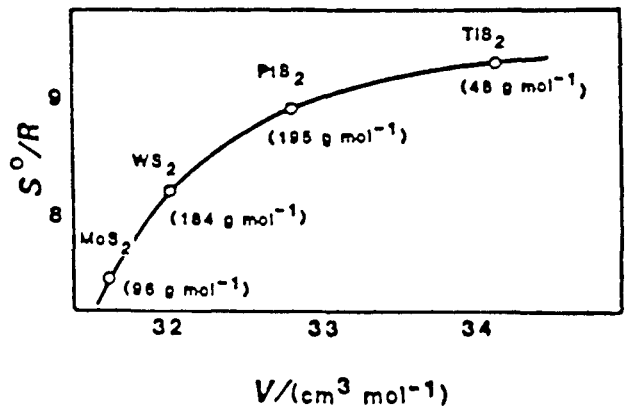
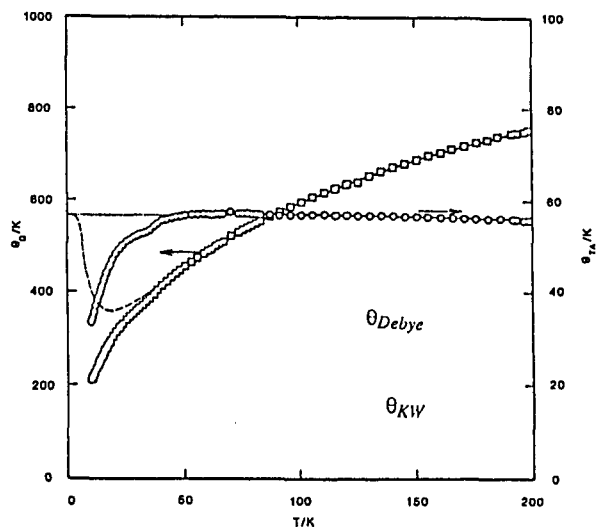


Fig. 2. Correlation of entropies and molar volumes. The values in parentheses are molar masses of the cations; hence, the monotonic trend would fail for the Latimer relationship.

Fig. 3. Variation of  $\theta_D$  (□) and  $\theta_{KW}$  (o) with temperature for deerite [10]. The extrapolated  $\theta_D$  calculated from  $\theta_{KW}$  is shown dashed.



### THE PHONON DISTRIBUTION MODEL

Komada and Westrum developed a new model for the phonon distribution [10-12] distinguished by a single characteristic temperature as a fitting-parameter for the analysis and/or prediction of the thermodynamic properties. Although the equation derived from the model to calculate the lattice heat capacity at constant volume is somewhat lengthy, it is simple enough to manage even on a microcomputer. Three computer programs written in FORTRAN IV were prepared to evaluate apparent characteristic temperatures from given heat-capacity data, to predict lattice heat capacities from the given characteristic temperatures, and to compare the predicted and given (possibly experimental) heat capacities. These programs ensure the convenient analysis of heat-capacity data. The model has already proven its utility in treating experimental data on eight compositions of matter ( $Mn_{0.63}Cr_{0.37}As$ , deerite, grunerite, and some scapolites) [10].

Although time does not permit a detailed description of the model, it is composed of four major contributions corresponding to transverse acoustical, longitudinal acoustical, transverse optical, longitudinal optical, and—if appropriate—discrete internal vibrational modes [10,11]. It takes account of the influence of mass distributions and the non-spherical shape of the first Brillouin zone on the phonon/density distribution. An isometric molar lattice heat-capacity equation is derived on the basis of the phonon-density distribution model restrained to the harmonic oscillator approximation. Although the equation contains several parameters which may be evaluated from chemical and crystallographic data for the particular compound—or be filled by default values—a single remaining (constant) parameter  $\theta_{KW}$  (similar in some respects to the Debye characteristic temperature) is used to fit the heat-capacity curve. The test of the approach is in the constancy of the  $\theta_{KW}$  itself. In Figure 3 this is tested against experimental data for deerite. It is evident that above 30 K the  $\theta_{KW}$  is nicely linear and constant in marked contrast to the meandering of the Debye characteristic temperature,  $\theta_D$ . At the lowest temperatures both  $\theta$ 's respond to anomalous behavior in the sample.

Many applications of this method have already been made and show the tremendous power of the approach. These include resolution of Schottky contribution (despite *excess* contributions over most of the experimental region), magnetic transitions in minerals, and even the resolution of electron delocalization phenomena. Correction for anharmonicity has proven practicable.

### COMPARISON OF VOLUMETRIC PRIORITY AND PHONON-DENSITY DISTRIBUTION APPROACHES

A comparison of the resolution of Schottky contributions for six  $\gamma$ - $\text{Ln}_2\text{S}_3$  compounds by the "Volumetric Priority Method" based on interpolation between heat capacities of lanthanum and gadolinium sesquisulfides (neither of which have Schottky contributions) and the same data treated by the "Phonon-Density Distribution Method" is presented in Figure 4. Taking into account that the excess heat capacity attributable to the Schottky contribution is typically less than 10% of the total, the close agreement between the two methods—despite the very significant difference in their theoretical approaches (*e.g.*, in their incorporation of temperature dependence)—argues for the correctness of both. This is further verified by the comparison of the Schottky levels derived from fitting the combined curves and comparing these values with the crystalline electric fields splitting values obtained by spectroscopy [5,13,14]. The excellence of the agreement provides the final justification for both approaches.

### OTHER MODELS

Because the estimation of lattice heat capacity is important in resolving excess heat capacities, in extrapolating heat-capacity curves beyond the temperature region measured, and in predicting the heat capacity of related compounds, the Debye model is still often used for these purposes. Lattice heat capacity is fully described by essentially a single variable, the Debye characteristic temperature, which can be treated as a parameter determined by fitting the model to the heat-capacity curve. However, the model generally provides an accurate estimate only for the extremely low-temperature region (typically below 1/50 of the Debye characteristic temperature).

The Born-Von Kármán formalism [8,9] facilitates evaluation of an accurate density of vibrational modes as a function of frequency and the estimation of a more accurate lattice heat capacity. The number of force constants in such procedures is, however, so large that many phonon models have been used to reduce the number of parameters. But since even these phonon models require roughly ten parameters to represent the phonon distribution function for a simple compound and require additional data from sophisticated, slow neutron scattering experiments, etc., they are quite impractical for the routine analyses of heat-capacity data.

Many others have sought a reasonably simple and accurate model of phonon distribution for practical use. A popular method is to express lattice heat capacity as a combination of Debye and Einstein functions. That is, two transverse acoustical modes (sometimes degenerate) and one longitudinal acoustical mode are approximated by a parabolic distribution which leads to a Debye function.

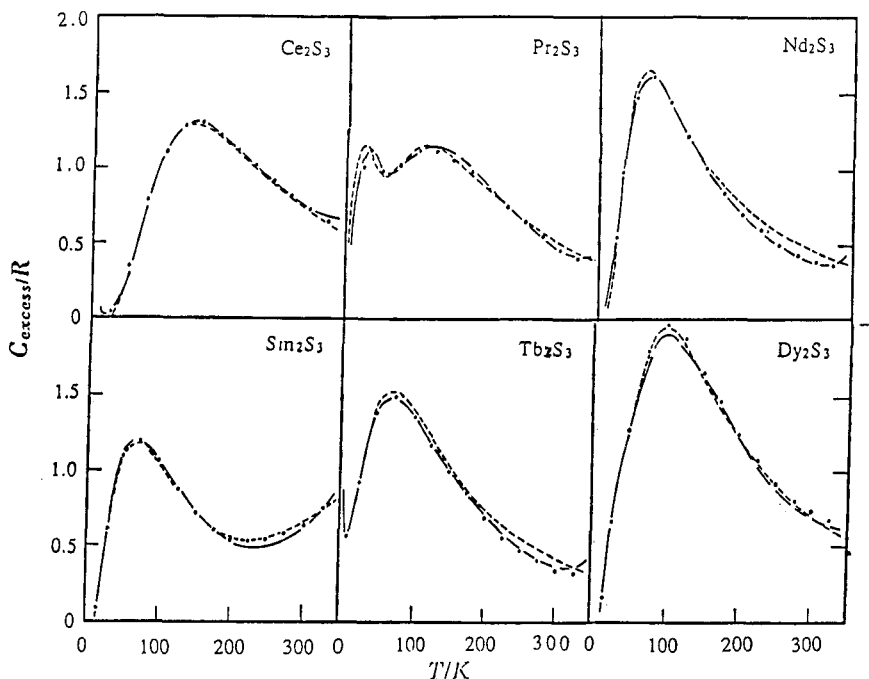


Fig. 4. Comparison of Schottky contributions obtained from Volume Priority - - - - and Phonon-density distribution — • — methods.

The more recent Kieffer model [15,16] has been useful in mineralogy. Kieffer's theoretical and experimental correlation of the lattice vibrations of minerals takes into account the many factors involved and discusses particularly the analysis of the vibrational contribution. Though such semi-empirical approaches are very useful, especially for prediction of the lattice heat capacity from elastic and spectroscopic data, it is very difficult to derive from them a representative characteristic temperature and, therefore, useful relationships like the Lindemann equation or the Grüneisen relation are not applicable unless each vibrational mode is considered independently [7]. Another problem with such methods is the impracticality of fitting them to the experimental heat-capacity curve because of the many parameters involved. Therefore, the application of these methods to the analysis of calorimetric data is confined to the comparison between predicted and experimental heat capacities when elastic and spectroscopic data are available.

### EXTENSION TO THE VITREOUS PHASE

Another aspect of phonon-density distribution yields an analysis of the vitreous structures and enables the development and determination of primitive volumes for vitreous materials and thereby their inclusion within the Komada-Westrum approach. The first derivation from first principles of an adequate, practicable equation was published by Barker and Martin in 1959 [17]. The Debye functions can be improved to fit essentially within experimental uncertainties by introducing  $W(v)$  versus  $v_a$  in place of Debye's constant  $W(0)$ ; i.e. by representing velocity dispersion in  $g_o(v, v_a^*)$  versus  $v$ . Such dispersion formulas were derived and published by Schrödinger [18] in 1926 but the dramatic improvement in them has not been appreciated and they have been so neglected and underappreciated by reviewers and monograph writers that they have been rederived and evaluated independently of Schrödinger in 1959 [17] and again by Kieffer in 1979 [15].

Derivation of the dispersion formulas follows from Brillouin's fundamental description of wave propagation [19]. Two comprehensive reviews were available to us during our project: those of Blackman [20] and of de Launay [21]. Blackman reviews not only his many earlier papers but evaluates a dispersion formula similar to Schrödinger's for which he cites Schrödinger's reference to an earlier paper by Born and von Kármán [9].

We were not the first to seek structural information from  $C_p(T)$  of glasses; between 1945 and 1957, before any data suitable for such inferences was available, Tarasov [22] published a series of papers in which he claimed to show that "specific heat functions for chain-like structures" could be found in "temperature dependence of the specific heat of vitreous  $B_2O_3$ ," for example, and that similar evidence of "layered" structures could be found in certain silicate and borate glasses. His several papers are reviewed collectively and expanded in a book [23]. His curve-fitting exercises which failed to take due account of velocity dispersion cannot lead to credible results.

Barber and Martin's equation takes into account velocity dispersion of both transverse and longitudinal acoustical phonons. Their formula

$$g(v, v_a^*) = 72N\bar{a} \{ \sin^{-1} [\pi v \bar{a} / W(0)] \}^2 / [ \pi^2 W(0) \{ 1 - [\pi v \bar{a} / W(0)]^2 \}^{1/2} ] \quad (1)$$

is significantly better than the Debye distribution. The corresponding parameter  $\bar{\theta} = 2\theta_D/\pi$ , and the density of states at  $v_a^*$  is greater by  $(\pi/2)^3 = 3.876$  and zero at  $v_D$ .

The Barber and Martin values of  $C_v(v, v_a^*)$  are best compared with the corresponding Debye formulation in a plot of  $\ln(C_v x^3 / 3R)$  versus  $\ln(1/x)$  as in Figure 5. Such curves can be rescaled simply by adding  $\theta$  to the latter coordinate and subtracting  $\theta^3$  from the former. Conversely, the plot can be brought into coincidence (within experimental uncertainty) with a theoretical function of  $x$  by appropriate translations along both axes to ascertain the values of  $\theta_a$  which best represent measurements of  $\ln C_v$  versus  $\ln T$ .

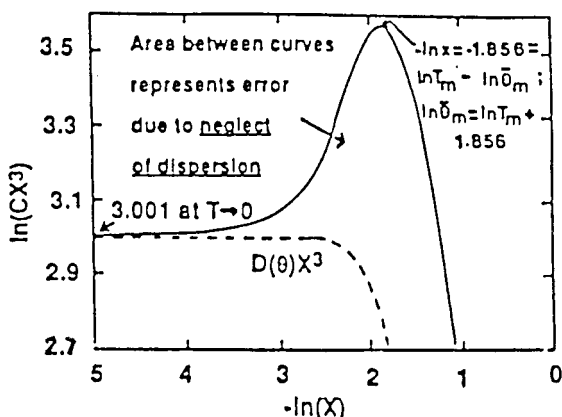


Fig. 5. Reference curve. Barber theoretical curve with dispersion ———. Debye curve without dispersion - - - - - ( $C = C_v/3R$ ).

Velocity dispersion entirely accounts for the maximum at  $\ln x_m$  in the dispersion function. Its neglect by Debye yields a curve without a maximum.

The analysis of experimental  $C_v$  versus  $T$  begins by plotting  $\ln(fC_v/3RT^3)$  versus  $\ln T$  where  $f$  is the fraction of primitive cell volume represented by  $C_v$ . When experimental data are functions of acoustic phonons only, such plots approximate the reference curves in shape and by judicious choice of coordinate scales the maximum can be brought to near coincidence with that of a reference curve without modifying the shape of the experimental curve.

Although the general approach outlined here has been applied to crystalline tungsten, copper, and to various  $\text{SiO}_2$ -phases, we will summarize only briefly the main results on crystalline and vitreous alkali disilicates in Tables 1, 2, and 3. The size of the primitive cell is the most important derivative result for our application and enables us to apply the Komada/Westrum approach to the vitreous phase. Table 1 provides the characterization of the alkali disilicate samples studied. They were in the form of case annular cylinders to fit over the heater/thermometer well in the calorimeter.

**Table 1. Characterization of alkali disilicates**

Sample <sup>a</sup>	$x$	$\frac{m}{g}$	$\frac{M_{ns}^b}{g \cdot \text{mol}^{-1}}$	$\frac{M_s^c}{g \cdot \text{mol}^{-1}}$	$\frac{\rho}{g \cdot \text{cm}^{-3}}$
$\text{Li}_2\text{O} \cdot x\text{SiO}_2(\text{v})$	2.086	192.4010	155.183	150.051	2.308
$\text{Na}_2\text{O} \cdot x\text{SiO}_2(\text{v})$	2.034	184.4097	184.191	182.149	2.485
$\text{K}_2\text{O} \cdot x\text{SiO}_2(\text{v})$	2.100	188.2779	220.374	214.365	2.472
$\text{Li}_2\text{O} \cdot x\text{SiO}_2(\text{x})$	1.940	116.7901	146.446	150.051	2.430
$\text{Na}_2\text{O} \cdot x\text{SiO}_2(\text{x})$	1.989	109.0478	181.488	182.148	(2.50)
$\text{K}_2\text{O} \cdot x\text{SiO}_2(\text{x})$	2.037	99.9374	216.588	214.365	2.410

<sup>a</sup> v = vitreous, x = crystalline

<sup>b</sup> molecular mass of non-stoichiometric sample

<sup>c</sup> molecular mass of stoichiometric compound

**Table 2. Adjusted thermophysical properties of vitreous and crystalline disilicates at 298.15 K for  $\text{M}_2\text{O} \cdot 2\text{SiO}_2$  compositions**

Composition	$C_p/R$	$S/R$	$H/(R \cdot K)$	$\phi/R$
$\text{Li}_2\text{O} \cdot 2\text{SiO}_2(\text{v})$	17.95	16.30	2762	7.04
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2(\text{v})$	19.21	20.67	3277	9.68
$\text{K}_2\text{O} \cdot 2\text{SiO}_2(\text{v})$	19.49	23.26	3506	11.60
$\text{Li}_2\text{O} \cdot 2\text{SiO}_2(\text{x})$	17.34	14.65	2568	6.04
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2(\text{x})$	19.02	19.47	3176	8.82
$\text{K}_2\text{O} \cdot 2\text{SiO}_2(\text{x})$	19.38	23.00	3478	11.33

**Table 3. Summary of  $\bar{\theta}$  values <sup>a</sup> for vitreous and crystalline alkali disilicates**

Composition of primitive volume, $V^*$	$\bar{\theta}_m(0)^b$	$f^c$	$n^d$	$\theta_t^e$	$\theta_l^e$	$\bar{\theta}_a(0)^c$	$\Delta\theta(T)^c$	$\frac{\lambda^{*cell f}}{A}$
$n(\text{Li}_2\text{O} \cdot 2.086 \text{ SiO}_2)(\text{v})^g$	109.5	2.20	4	98.9	145.3	112.4	4.6	12.44
$n(\text{Na}_2\text{O} \cdot 2.034 \text{ SiO}_2)(\text{v})$	86.5	1.88	2	81.0	133.1	95.6	6.1	12.30
$n(\text{K}_2\text{O} \cdot 2.100 \text{ SiO}_2)(\text{v})$	67.1	1.97	2	63.7	112.1	76.9	6.1	13.30
$n(\text{Li}_2\text{O} \cdot 1.94 \text{ SiO}_2)(\text{x})$	188.	1.15	1	(W <sub>t</sub> , W <sub>l</sub> not known)	(W <sub>t</sub> , W <sub>l</sub> not known)	(W <sub>t</sub> , W <sub>l</sub> not known)	(W <sub>t</sub> , W <sub>l</sub> not known)	(W <sub>t</sub> , W <sub>l</sub> not known)
$n(\text{Na}_2\text{O} \cdot 1.989 \text{ SiO}_2)(\text{x})$	128.	1.22	1					
$n(\text{K}_2\text{O} \cdot 2.037 \text{ SiO}_2)(\text{x})$	99.	0.93	1					

<sup>a</sup> From corresponding values of  $n$  and  $\bar{\theta}_a(0)$  calculated from our data

<sup>b</sup> From graphical analysis

<sup>c</sup>  $f$  is the number of gram formula masses per primitive cell

<sup>d</sup>  $n$  is the integer nearest  $f$  is plausible but not always verifiable in values of  $\bar{\theta}_a$  (apparent) especially in cases where both  $n$  and the total number of modes are large

<sup>e</sup> From  $W_t, W_l$  and  $V_j$ ;  $t$  = transverse,  $l$  = longitudinal.  $\bar{\theta}_a$  is required in the Barber model to separate the acoustic contribution from the cryogenic heat-capacity results. The optic contribution frequencies are the difference between the experimental and the calculated acoustic curves.

<sup>f</sup>  $\lambda^{*cell} \approx 2a \text{ cell}$

<sup>g</sup> (v) indicates glass; (x) indicates crystal

The values of the smoothed thermophysical properties given in Table 2 adjusted to stoichiometric composition at selected temperatures are obtained by computer smoothing of the heat-capacity data and integration both by hand and by computer of these values to get the other reported thermophysical properties. The adjustment to stoichiometric end member composition was made by utilizing the heat capacities of vitreous silica and of  $\alpha$ -quartz for adjustment of the vitreous and crystalline materials, respectively. The entropy (increments) and derived properties for the vitreous phases are those above zero Kelvin. It is presumed that the zero point entropies for these phases are probably deviant from the third law of thermodynamics.

Even without knowledge of  $V^*$  from atomic structures in either crystals or glasses, it is possible by inference from dispersion maxima alone to show that  $V^*$  equals one gram formula volume (gfv) in each of the three crystalline materials and  $V_c^*$  equals at least two gfv's in the glasses shown in Table 3. Moreover, by application of the Barber and Martin model to our alkali disilicate systems, the experimental low-temperature heat capacity yields detailed information about important physical parameters such as the volume of the primitive cell, and the interatomic spacing (which governs the wavelength). The glassy forms of binary disilicates have a peak in their frequency distribution at much lower relative frequencies than do the corresponding crystalline materials, i.e.,  $\bar{\theta}_m < \bar{\theta}_m(x)$  and is probably related to the very open structure of these materials. The  $\bar{\theta}_m$  values cannot be verified by the  $T^3$  law for any glasses at any  $T$ , but they can be inferred from dispersion theory at  $T_m \sim \theta(0)/6$ . The corresponding values of  $\bar{\theta}_m(0)$  are uniformly higher in the crystals than in the glasses as required by hypothesis.

Novel derived contributions to the science of glasses are that meaningful values are provided for the several fundamental parameters listed in Table 3. These are important characteristics of elastic solids and correlate with other elastic and thermal properties. In contrast, the conventional Debye theta, being an arbitrary representation of thermal effects without distinction of acoustic (i.e., elastic) from optic modes, lacks such relevance to the other parameters of elasticity. Primitive volumes in these glasses are only about twice that of those for crystalline (Na, K) materials with one exception (Li,  $n = 4$ ). This implies remarkably small differences between ordering in glasses and in crystalline materials—no more than could be expected by mixing two well-ordered polymorphs of the same composition.

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