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Thermal expansion in insulating materials

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A model of thermal expansion in terms of the Morse potential which was developed earlier for low temperatures is extended to high temperatures and applied to a semi-empirical calculation of thermal expansion in insulating materials. In this model, the localized quantum mechanical solutions of the Morse potential are combined with the Debye model to give a localized-continuum description of thermal expansion. A set of empirical rules is developed for characterizing the interatomic potential in terms of the Morse potential. These are then applied to the quantitative calculation of thermal expansion in the alkali halide crystals and a group of binary high temperature materials with the aid of the known crystal structures, compressibilities, and Debye temperatures of these materials. Good agreement between calculated and experimental values is obtained for temperatures ranging between 0 K to values near the melting points. A discussion of the underlying basis of the empirical rules is given as well as their likely applicability to a wide range of insulating materials.

1. Introduction

An indication of the importance of thermal expansion as a property of materials is the number of papers which have appeared on the subject. A large number of publications have treated the subject from many different points of view, using theoretical, experimental, and empirical approaches. While considerable progress has been made in understanding thermal expansion in materials, it would be quite desirable to be able to estimate or predict the thermal expansion of a wide range of materials by means of a general but simple technique which requires little if any experimental input. This is particularly true of insulating and ceramic materials which display not only a wide range of values of thermal expansion coefficients, but also of bond types and other physical properties as well.

This work will report on progress toward reaching this goal which has made use of a localized-continuum model of thermal expansion developed earlier for studying the elastic moduli and thermal expansion in cubic metals [1]. In this model, the quantum mechanical solutions for the localized interatomic potential are thermally averaged and combined with the Debye approximation. The thermal expansion arises from the nonsymmetric property of the interatomic potential. Thus the thermal expansion in this model is determined by a few parameters which characterize the interatomic potential. In actual calculations, the thermal expansion has been determined by making use of the Morse potential as a model interatomic potential. Since the quantum mechanical solutions for the Morse potential are known exactly, it is possible to construct a detailed theoretical description of the thermal expansion if a fit of the Morse potential to the actual interatomic potential is made. It is rather easy to show that at low temperatures, according to this approach, the coefficient of thermal expansion has the same functional form as the specific heat, and the multiplicative constants involve the parameters of the effective Morse potential.

This approach is promising in that the thermal expansion curve can be predicted, in principle, from a few parameters characterizing the interatomic potential. The accuracy of the predicted curves should be quite good up to temperatures approaching the melting points. Thus, the problem of predicting the thermal expansion is reduced to one of characterizing the interatomic potential with as little extra experimental information as possible.

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2. Thermal expansion in terms of the Morse potential

The low temperature formulas for the thermal expansion $\Delta l/l$ and the coefficient of thermal expansion $\alpha(T)$ were previously found [1] to be

$$\Delta l/l = (3kT/2ar_nD)(T/\theta_D)^3 f(x_D) \qquad (1)$$

and

$$\alpha(T) = (3k/2ar_nD)(T/\theta_D)^3 g(x_D) \qquad (2)$$

where a and D are the inverse width and depth, respectively, of the Morse potential, θ_D is the Debye temperature, and $x_D = \theta_D/T$. The integrals $f(x_D)$ and $g(x_D)$ are given by

$$f(x_D) = \int_0^{x_D} \frac{x^3 \mathrm{d}x}{\mathrm{e}^x - 1}$$

and

$$g(x_D) = \int_0^{x_D} \frac{x^4 \mathrm{e}^x \mathrm{d}x}{(\mathrm{e}^x - 1)^2}$$

These formulas were derived within the framework of the Debye approximation which assumes that the Debye temperature is constant. In real materials, however, this quantity varies with temperature as a result of volume dependent anharmonic effects, and the actual vibrational frequency spectra are more complex in form than that of the Debye model. The variation in the Debye temperature can be as high as ± 10% or more, but the error involved in ignoring this temperature variation is much smaller than the other errors in the calculations which will be discussed later. Consequently, the Debye temperatures for all materials will be assumed to be constant, with the experimental values normally taken from extrapolation of elastic constant or specific heat data to 0 K. Since the nearest neighbour distance r_n usually appears with a, it is convenient to consider ar_n, the reduced inverse width of the potential, as a single variable. Generally the Equations 1 and 2 appear to be accurate up to about $0.7\theta_D$, and give the dominant contributions over the entire temperature range. The next step is to extend these formulas to higher temperatures. In the Appendix, it is demonstrated that the next most important contributions to these two quantities are given by

$$(\Delta l/l)_1 = (3kT/2ar_nD)(kT/4D)(T/\theta_D)^3 f_1(x_D) \qquad (3)$$

and

$$\alpha(T)_1 = (3k/2ar_nD)(kT/2D)(T/\theta_D)^3 g_1(x_D) \qquad (4)$$

where

$$f_1(x_D) = \int_0^{x_D} \frac{x^4(1 + \mathrm{e}^x)\,\mathrm{d}x}{(\mathrm{e}^x - 1)^2}$$

and

$$g_1(x_D) = \int_0^{x_D} \frac{x^5 \mathrm{e}^x(1 + \mathrm{e}^x)\,\mathrm{d}x}{(\mathrm{e}^x - 1)^3}$$

At high temperatures, Equations 3 and 4 are fractional corrections to Equations 1 and 2, respectively, of magnitude $kT/2D$ and kT/D. In most cases, these two contributions to the percent thermal expansion and the coefficient of thermal expansion are accurate representations of experimental data at temperatures approaching the melting point. Consequently, no further refinements of the formulas will be made for the succeeding analysis, although it should be recognized that still higher order corrections can probably be made most easily by direct use of the solutions of the Morse potential rather than by considering further terms in the series expansion.

The importance of these formulae lies in their ease of interpretation (the value of D is easily fixed by the high temperature behaviour of Equation 3 or 4, and the width of the potential can then be determined by the leading terms in Equation 1 or 2), and in the fact that they are derived from the exact solutions of a realistic interatomic potential. Application of the theory to real materials now requires that a connection between the Morse potential and the bottom of the interatomic potential be made, since thermal effects are unaffected by the shape of the potential well further up. As might be expected intuitively, some detailed calculations indicate that the thermal expansion is primarily determined by the overall shape of the potential well, and not by fine details of its point-to-point functional dependence.

3. Thermal expansion in the alkali halides

The most obvious starting point for the analysis of thermal expansion in insulators is the alkali halide crystals, since they most closely represent the ideal ionic model. Cohesion in such crystals has been studied for many years and a considerable amount of empirical information has been accumulated. As has been previously discussed [1], the interatomic potential minimum in metals usually does not coincide with the nearest neighbour distance, a fact that introduces some analytical complications. This problem does not occur to any significant extent in insulators since the cohesive energy is well represented by the interatomic potential. Therefore the Morse potential minimum is essentially at the nearest neighbour distance, and the potential, itself, has the form

$$V(r) = D(1 - \mathrm{e}^{-a(r-r_n)})^2 \tag{5}$$

For simplicity, we will represent the interatomic potential in the alkali halides by means of the Born potential

$$V(r) = -A/r + B/r^m \tag{6}$$

in which the attractive Coulomb term is counterbalanced by a simple power law repulsive term. The reasons for using this simple form for the potential energy lie primarily in its extreme simplicity and in the fact that more sophisticated potentials do not appear to increase the accuracy of the calculation to any significant extent. As is well known, at the equilibrium position (potential minimum), Equation 6 reduces to

$$V(r_n) = A/r_n(1 - m^{-1}) \tag{7}$$

so that

$$B = Ar_n^{m-1}/m$$

where A is given by

$$A = b^2e^2M,$$

M being the Madelung constant, e the electronic charge, and b the largest common factor in the valences of the atoms. The repulsive exponent m is directly related to the volume compressibility σ by the equation

$$m - 1 = 9\beta_0^3/\sigma A \tag{8}$$

where β_0^3 is the molecular volume.

Although these equations are simple in form and easy to apply, it is necessary to make the connection between the two Equations 5 and 6 in order to actually calculate the thermal expansion of the alkali halides. Qualitatively speaking, it is evident that the depth of the potential well given in Equation 6 (representing the cohesive energy per ion in the crystal) is not the same as the depth D in the thermal potential energy well in Equation 5. This is because the latter is the energy associated with the maintenance of the crystalline or solid state, and this is an order of magnitude smaller than the cohesive energy. The cohesive energy is defined as the energy necessary to completely separate all the ions in the crystal, whereas complete vaporization of the crystal usually results in a gas of diatomic molecules in the alkali halides which usually polymerize into larger aggregates. The energy of diatomic dissociation in the alkali halides is the largest contribution to the cohesive energy and is an order of magnitude greater than the energy associated with the solid phase at 0 K, i.e. the energy necessary to raise the crystal up to the melting point plus the heat of fusion. The great disparity between this quantity E_s and the cohesive energy arises from this difference, and is the reason why the lattice dynamical energy which determines the thermal properties of solids is not directly related to the cohesive energy.

In line with these considerations, the most straight forward way to empirically determine the depth of the thermal potential well is to compare the magnitudes of E_s, the energy necessary to destroy the solid state starting at 0 K, and the cohesive energy. Available thermochemical data indicates that in the alkali halides, E_s is about 10% of the cohesive energy. This gives a convenient measure of the depth of the thermal potential in terms of a well known quantity. The inverse width a of the thermal potential can also be determined quite easily by noting that for the Morse potential, $a = -C/5K$, where C and K are the cubic and harmonic force, constants, respectively. Applying this condition to the potential, Equation 6, one obtains the result $(m + 4)/5r_n$ for the effective inverse width of the bottom of the potential well. These two empirical conditions

$$D = 0.1\,V(r_n) \tag{9}$$

$$ar_n = (m + 4)/5 \tag{10}$$

characterize the two parameters of the effective thermal Morse potential in terms of quantities which are well known for the alkali halides. Although the Born potential for these materials was characterized many years ago, this application

TABLE I Potential well data for the alkali halides

	m	$V(r_n)(K\,\mathrm{cal\,mol^{-1}})$	$D(eV\,\mathrm{ion^{-1}})$	ar_n
LiF	5.9	238	0.52	1.98
LiCl	8.0	196	0.43	2.40
LiBr	8.7	186	0.40	2.54
NaF	7.4*	216	0.47	2.28
NaCl	9.1	182	0.39	2.62
NaBr	9.5	173	0.38	2.70
KF	7.9	189	0.41	2.38
KCl	9.7	165	0.36	2.74
KBr	10.0	158	0.34	2.80
RbF	8.4*	180	0.39	2.48
RbCl	9.9*	158	0.34	2.68
RbBr	10.0	151	0.33	2.80

*Interpolated values.

TABLE II Calculated and observed percent thermal expansion for various alkali halide crystals. The experimental values are in parentheses.

	T(K)									
	50	100	150	200	250	293	400	500	600	700
LiF	−0.466	−0.427	−0.368	−0.267	−0.131	0.000	0.377	0.767	1.180	1.614
	(−0.481)	(−0.453)	(−0.378)	(−0.275)	(−0.140)	(0.000)	(0.405)	(0.805)	(1.227)	(1.678)
LiCl	−0.703	−0.639	−0.512	−0.350	−0.168	0.000	0.440	0.872	1.318	
		(−0.706)	(−0.558)	(−0.381)	(−0.183)	(0.000)	(0.491)	(0.993)	(1.539)	
NaF	−0.612	−0.567	−0.463	−0.320	−0.155	0.000	0.407	0.813	1.235	1.670
	(−0.547)	(−0.500)	(−0.409)	(−0.285)	(−0.137)	(0.000)	(0.381)	(0.759)	(1.159)	(1.584)
NaCl	−0.813	−0.712	−0.550	−0.360	−0.155	0.000	0.514	0.912	1.372	1.830
	(−0.772)	(−0.666)	(−0.521)	(−0.352)	(−0.168)	(0.000)	(0.448)	(0.896)	(1.371)	(1.878)
NaBr	−0.912	−0.774	−0.592	−0.402	−0.185	0.000	0.574	0.922	1.392	1.867
	(−0.836)	(−0.710)	(−0.551)	(−0.370)	(−0.173)	(0.000)	(0.461)	(0.925)	(1.427)	(1.970)
KF	−0.837	−0.741	−0.574	−0.392	−0.186	0.000	0.477	0.944	1.425	
		(−0.519)	(−0.410)	(−0.275)	(−0.131)	(0.000)	(0.353)	(0.723)	(1.137)	
KCl	−0.941	−0.803	−0.604	−0.386	−0.194	0.000	0.492	0.961	1.379	1.944
	(−0.723)	(−0.626)	(−0.487)	(−0.328)	(−0.155)	(0.000)	(0.407)	(0.818)	(1.259)	(1.735)
KBr	−1.042	−0.867	−0.643	−0.433	−0.204	0.000	0.516	1.015	1.520	2.043
	(−0.794)	(−0.693)	(−0.517)	(−0.345)	(−0.162)	(0.000)	(0.429)	(0.846)	(1.289)	(1.769)
RbCl	−1.097	−0.910	−0.687	−0.454	−0.211	0.000	0.544	1.063	1.593	2.143
	(−0.729)	(−0.622)	(−0.484)	(−0.326)	(−0.157)	(0.000)	(0.407)	(0.824)	(1.268)	(1.734)
RbBr	−1.118	−0.916	−0.689	−0.453	−0.214	0.000	0.535	0.931	1.583	2.128
	(−0.786	(−0.655)	(−0.503)	(−0.335)	(−0.158)	(0.000)	(0.421)	(0.829)	(1.258)	(1.713)

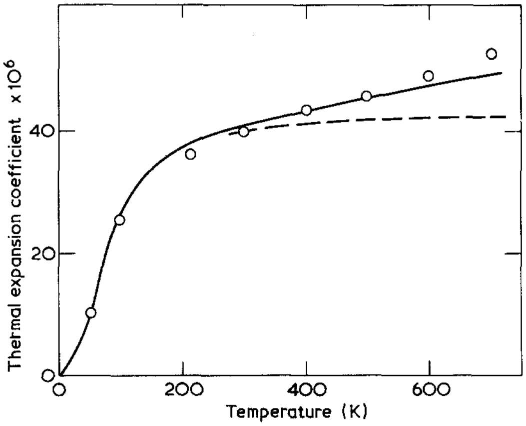

Figure 1 Theoretical versus experimental coefficient of thermal expansion for NaCl. The experimental points are the open circles and the solid curve is the theoretical result predicted by Equations 2 and 4. The dashed line is the contribution of the leading term Equation 2, which has the functional form of the specific heat and levels off to a constant value at high temperatures. The second term is linear in the temperature at high temperatures, and the fractional correction to the leading term at high temperatures is just kT/D. This easily fixes the depth of the potential well, and the width can be then determined from the dimensions of the leading term. Thus, the advantage of Equations 2 and 4 is that the dimensions of the effective potential well can be easily determined from experimental data, and vice versa.

to the determination of the thermal expansion is, however, entirely new. The calculation of thermal expansion of these materials using these parameters is easily accomplished using Equations 5, 6, 7, 8, 9 and 10, by using the known structures and Madelung constants of the alkali halides and the experimentally determined compressibilities [2]. The m values for the crystals for which Slater compressibilities were not determined were obtained by interpolating from the others. The potential well data so obtained for the alkali halides is listed in Table I, and the calculated percent thermal expansions for the alkali halides are compared with the experimental values obtained from the compilation of Touloukian *et al.* [3] in Table II. Fig. 1 illustrates a graphical comparison of the theoretical coefficient of thermal expansion for NaCl with the experimental values.

As can be seen by examining the results, the calculated values are in good agreement with the experiment, particularly since they represent an *a priori* calculation with a minimum of experimental input and no curve fitting. While this agreement tends to confirm the validity of Equations 9 and 10 as a method for choosing the parameters of the interatomic potential, the appendix discusses an independent method for checking the values of the parameters. The experimental values for the Debye temperatures are compared with a simple relation which approximates the Debye temperatures and which involves only the parameters of the interatomic potential and the atomic masses. The generally good agreement between the two sets of values gives further confirmation to the validity of the values obtained from Equations 9 and 10.

4. Thermal expansion in high temperature materials

The alkali halides represent a particularly simple group of materials for applying the model for thermal expansion which has been presented here since they most closely correspond in their properties to the classical ionic model. In expanding the analysis to a broader category of insulating materials, a basic question concerns the applicability of an ionic interatomic potential to materials which are generally less ionic than the alkali halides. The question of bonding mechanisms in materials is a complex one which is still the subject of lively debate, but the only question which need concern us here is whether the potential in Equation 6 together with the empirical criteria, Equations 9 and 10 can be used to characterize the shape of the bottom of the interatomic potential in a larger class of materials than the alkali halides. This question is not necessarily directly related to the nature of the overall bonding mechanism, and an affirmative answer would afford a greatly simplified means of analysing thermal expansion in a wide range of materials without a cumbersome analysis of bond type for each particular case.

The most direct way to examine this question would be to make use of thermochemical data for a wide range of materials as was done in the case of the alkali halides. Unfortunately, such data are usually unavailable, or are too fragmentary to be definitive. Because of this, the question will be examined from a somewhat more heurestic point of view. A group of insulators with high melting temperatures and different crystal structures, with bond types ranging from predominantly ionic to predominantly covalent will be treated according to the methods previously used for the alkali halides. The parameters of the potential wells so obtained will be used to compute approximate Debye temperatures which are compared in the appendix with the experimental values. Agreement comparable to that found in the alkali halides is taken as an indication that the potential well parameters found for these materials are valid, and they are then used to compute the thermal expansions. The relatively good agreement between the calculated and observed values is consistent with the conclusion that the simple empirical approach to thermal expansion developed for the alkali halides is applicable to a wide range of insulating materials.

The application of the potential in Equation 6 to any class of materials is quite simple so long as the crystal structure and associated Madelung constant, volume compressibility, and atomic valences are known. By concentrating on atomic valences rather than effective charges, the whole question of ionicity is avoided and the potential can be used for completely covalent materials where the idea of ionic charges is meaningless. Of the required quantities, the only one which is not generally available is the volume compressibility. Because many insulators are much harder than the alkali halides, static compressibility measurements such as were made on them many years ago are usually much more difficult to accomplish and are probably less reliable. The compressibility can also be obtained from elastic constant measurements which are much more reliable, but these measurements are available for only a limited number of materials. Although the calculated cohesive energy is quite insensitive to the magnitude of the repulsive exponent, it is evident from Equation 10 that the effective width of the thermal potential is sensitive to the value of m so that a means of accurately estimating its value is needed when accurate compressibilities are not available.

In the early days of the application of the Born model, it was usually assumed that the repulsive exponent was only dependent upon electronic configurations and not the valences of the constituent atoms in the crystal. The m values for the alkali halides and other materials composed of monovalent atoms could then be used for materials having the same electronic configurations but larger valences in the constituent atoms. However, more recent compressibility measurements indicate that this assumption is not correct. Table III contains compressibility data for a group of oxide materials having relatively high melting points and hardness which were obtained from elastic constant and static compression measurements, references [4, 5] for TiO_2, reference [6] for Al_2O_3, reference [7] for MgO, and reference [8] for CaO, SrO and BaO. The table compares the values of m obtained from these measured compressibilities using Equation 8 with the m values for the corresponding alkali halides having the same anion–cation electronic configurations and which are labeled m_1. As can be seen from the table, the calculated m values based upon the experimental compressibilities are very different from the values m_1. This is not surprising since one would expect materials which are an order of magnitude harder than the alkali halides to have a much higher percentage of their cohesive energies included in the repulsive energies, as indicated by Equation 7. Instead of an equality between the values of m and m_1, the data in Table III indicate that $m-1$, which is given by Equation 8, scales according to the average valence of the atoms in the material. If q is the average valence of the atoms and m_1 is the monovalent repulsive exponent for the same anion–cation electronic configurations, then

$$m_q - 1 = (m_1 - 1)/q \qquad (11)$$

The last column in Table III corresponds to m_q for each of the listed materials and it is evident that there is a very good correspondence between these numbers and the values of m obtained from the compressibility data. The compressibility data

TABLE III Repulsive energy data for various oxides

	$\sigma(10^{-13}\ \mathrm{cm^2\ dyne^{-1}})$	m (calc)	m_1	$1 + (m_1 - 1)/q$
TiO_2	4.73	3.6	7.9	3.6
Al_2O_3	3.99	4.2	7.4	3.7
MgO	6.54	4.3	7.4	4.2
CaO	8.8	5.2	7.9	4.5
SrO	8.3	6.9	8.4	4.7
BaO	17.4	4.7	8.7	4.8

for the last three materials in the table were obtained from static compression measurements, and considering the difficulty in this type of measurement, the values of m obtained from Equation 11 may be more accurate than those obtained from the experimental data.

Making use of Equation 11 in addition to those already used for the alkali halides, it is a simple matter to develop potential well data for a wide range of insulating materials with readily available information. In order to test this procedure, we have chosen a group of five high temperature insulators which vary widely in physical characteristics including bonding mechanism, crystal structure, hardness, etc. These particular materials were chosen because of their range of properties, and the reliability of the experimental thermal expansion data and Debye temperatures for each of them. The materials are placed in order of decreasing ionicity, with MgO being the most ionic and diamond the least. The calculated potential well data are listed in Table IV for these materials. The values of m_q for the first three materials were obtained from Equation 11 rather than from the experimental compressibilities partly for consistency, and partly because m_q should be obtained from the compressibilities extrapolated to zero temperature and pressure, which cannot be done from a single measurement. Since there is little difference between the two sets of values, this choice does not produce any important differences with the experimental data. The data in Table IV are used to calculate approximate Debye temperatures which are compared with the experimental values in the appendix and calculated percent thermal expansions which are compared in Table V with observed values taken from reference [3].

The calculated Debye temperatures in the appendix agree with the experimental values about as well as do those for the alkali halides, which supports the conclusion that the potential well parameters for these materials listed in Table IV are reasonably accurate. This conclusion is further supported by the good agreement between calculated and observed thermal expansions in Table V. Since the calculational procedure used here gives what is basically an average potential well for non-cubic crystals, the average or polycrystalline thermal expansions for TiO_2 and Al_2O_3 are compared with the calculated values. Since TiO_2 (rutile) has about a 30% anisotropy in the thermal expansion in the two different directions, the results indicate that this procedure is still accurate for anisotropies at least that large. (In Al_2O_3 the anisotropy is considerably less).

TABLE IV Potential well data for various high temperature materials

	m_q	$V(r_n)$(K cal mol^{-1})	D(eV ion^{-1})	ar_n
MgO	4.2	834	1.81	1.64
Al_2O_3	3.7	3158	2.74	1.54
TiO_2	3.6	2339	3.38	1.52
SiC	2.6	2854	6.19	1.32
Diamond	2.2	1560	6.77	1.25

The most interesting observation which can be made from the results in Table V is that the accuracy of the calculated results is only slightly poorer than in the alkali halides and virtually uniform for each of the materials, in spite of the fact that beginning with the alkali halides, proceeding to MgO, and on to diamond, the materials represent virtually every possible bonding mechanism. This suggests, rather surprisingly, that the empirical procedure developed for determining the shape of the thermal part of the interatomic potential in the alkali halides, which are decidedly ionic, appears to be applicable to other insulators, regardless of bond type. However, it must be remembered that while $V(r_n)$ represents the cohesive energy per ion in a purely ionic crystal, it is purely an artifice of the calculation in any other type of crystal. Consequently, in an ionic crystal, $0.1\,V(r_n)$, representing the depth of the effective thermal potential, is a small part of the cohesive energy. In a covalently bound crystal, however, one would expect that the shape of the interatomic potential more closely approximates the shape of the Morse potential, so that $0.1\,V(r_n)$ should approximate the cohesive energy, itself. It is interesting to observe, in line with this, that $0.1\,V(r_n)$ for SiC and diamond, as obtained from Table IV, is 285 Kcal mol^{-1} and 156 Kcal mol^{-1}, respectively, which compare favorably with quoted [9] values of 283 Kcal mol^{-1} and 170 Kcal mol^{-1} for their cohesive energies.

5. Conclusions

A theoretical procedure for calculating the thermal expansion in solid materials has been developed using the Morse potential as an approximation to the bottom or thermal part of the actual interatomic potential. In terms of the Morse potential, the theory of thermal expansion is relatively simple

TABLE V Calculated and observed percent thermal expansion for various high temperature materials. The experimental values are in parentheses

	T(K)										
	100	200	293	400	600	800	1000	1200	1400	1600	1800
MgO	−0.105	−0.071	0.000	0.110	0.369	0.630	0.917	1.208	1.404	1.808	
	(−0.130)	(−0.080)	(0.000)	(0.128)	(0.380)	(0.656)	(0.944)	(1.244)	(1.558)	(1.880)	
Al_2O_3 *	−0.067	−0.046	0.000	0.075	0.244	0.432	0.628	0.830	1.035	1.243	1.456
	(−0.066)	(−0.038)	(0.000)	(0.075)	(0.225)	(0.388)	(0.565)	(0.754)	(0.952)	(1.158)	(1.370)
TiO_2 *	−0.085	−0.053	0.000	0.074	0.227	0.389	0.557	0.725	0.895		
	(−0.130)	(−0.070)	(0.000)	(0.083)	(0.251)	(0.435)	(0.623)	(0.819)	(1.020)		
SiC	−0.037	−0.025	0.000	0.038	0.125	0.222	0.322	0.424	0.528	0.633	0.741
	(−0.030)	(−0.024)	(0.000)	(0.041)	(0.126)	(0.219)	(0.321)	(0.431)	(0.546)	(0.668)	(0.795)
Diamond	−0.010	−0.008	0.000	0.018	0.075	0.149	0.233	0.323	0.415	0.511	
	(−0.012)	(−0.009)	(0.000)	(0.016)	(0.062)	(0.127)	(0.208)	(0.302)	(0.406)	(0.519)	

*Polycrystalline samples

to apply, involving only the two parameters of the Morse potential. Two leading terms in the theory are usually sufficient to describe the thermal expansion over temperatures covering the existence of the solid phase, and the use of just these two terms makes the calculations simple and easy to interpret. Because the fractional corrections Equations 3 and 4 to the thermal expansion and coefficient of thermal expansion at high temperatures are of magnitudes $kT/2D$ and kT/D, respectively, it is easy to establish the magnitude of D by inspecting experimental data, and from this, the magnitude of a from the leading terms in Equations 1 and 2. Therefore, the parameters of the potential can be determined rather easily from experimental data or vice versa.

The actual application of the theory to real materials requires that a connection be made between the Morse potential and the crystalline interatomic potential. This was done for the alkali halide crystals by relating the Born ionic potential to the Morse potential by empirical means. Making use of the known crystal structures and compressibilities of the alkali halides, the theory was used to calculate thermal expansions for these materials which are in good agreement with the experiment. The empirical approach was extended for application to other insulators as well, and applied to a group of high temperature materials having a wide variation in bonding mechanisms. The agreement was once again quite good, suggesting that the approach developed here may be applicable to the prediction of the thermal expansion properties of a wide range of insulating materials.

Appendix 1. Higher order corrections to the thermal expansion

It was previously demonstrated [1] that the diagonal matrix elements for the displacement associated with the Morse potential can be expressed in a convenient analytical form by making use of the asymptotic form of the digamma function as well as its recurrence relation. This procedure was only carried through to first order in the frequency, but is easily extended to second order. The result is

$$\langle r_k\rangle - r_n \simeq 2(at)^{-1}(k+\tfrac{3}{4}) + (at^2)^{-1} \times \sum_{i=1}^{k+1} (k+i+1/12) + O(t^{-3})$$

for the principal quantum number k, where $t = 4D/\hbar\omega$, and $\omega = a(2D/\mu)^{1/2}$ is the frequency of small oscillations. Obtaining the thermal expansion from this expression requires, as was discussed earlier, that a thermal average over all quantum numbers of this expression be made, and that this result be integrated over the complete Debye frequency spectrum. This procedure was carried out for the first order term, and it is basically the same for the second order term, except for some minor points which will be discussed here.

The form of the second order term is not one which is easily summed over all quantum numbers. However, this problem is easily remedied by observing that

$$\sum_{k=0}^{\infty}\sum_{i=1}^{k+1}(k+i+1/12) = [13/12 + \sum_{k=1}^{\infty}(2k^2+3k)]$$

The first or constant term is not thermally averaged and represents a small correction to the zero-point displacement. The last term, which is linear in the principal quantum number, is a small correction to the leading contribution which is linear in the frequency and which was treated earlier. This leaves the term in k^2 as the primary contributor to the thermal expansion from the second term in the displacement. Making use of the relation

$$\sum_{k=0}^{\infty} k^2 e^{-kx} = \frac{e^x(1+e^x)}{(e^x-1)^3}$$

the summation involved in the thermal average is easily made. Integration over the Debye frequency spectrum then results in two contributions, one of which gives small corrections to the leading terms in the thermal expansion in Equation 1 or 2, while the second results in the contributions of Equation 3 and 4. Aside from the negligible corrections, and contributions of higher order in the temperature which usually are not significant, the thermal expansion is well represented by the two contributions in Equations 1 and 3 or Equations 2 and 4.

Appendix 2. Approximate values of the Debye temperature from the parameters of the interatomic potential

Although there is no exact connection between the Debye temperature and the characteristics of the nearest neighbour interatomic potential in

TABLE VI Experimental Debye temperatures versus approximate calculated values for some simple metals

Metal	θ_D(K)	$(2\hbar/k)a(2D/m)^{1/2}$(K)
Al	430	543
Cu	340	347
Au	162	195
Pb	105	110
Ag	227	226
Th	165	171
Fe	477	501
K	91	137
Na	158	223
V	399	692
W	384	416

real crystals, an approximate connection is useful as a check on the parameters of the Morse potentials used in the calculations. The Debye temperature is proportional to a cutoff or maximum frequency of propagation in the crystal according to the assumptions of the Debye theory. A well known result for the linear monatomic chain is that the maximum frequency for this simple case is just twice the natural frequency of oscillation for one mass point attached to one of the springs. Using the corresponding frequency for the Morse potential, the Debye temperature for this case is given by $\theta_D = (2\hbar/k)a(2D/m)^{1/2}$. Although the situation in a three dimensional crystal is not the same, it is interesting to note from Table VI that this formula gives a good correlation with the experimental values for a group of simple metals whose Morse potential parameters had been determined previously [1].

TABLE VII Experimental Debye temperatures versus approximate calculated values for some insulating compounds

Compound	θ_D(K)	$(2\hbar/k)a(2D/\mu)^{1/2}$(K)
NaCl	322	328
LiF	732	670
LiCl	422	540
NaF	492	444
NaBr	225	280
KF	336	340
KCl	235	258
KBr	174	204
RbCl	165	202
RbBr	131	154
MgO	946	716
Al_2O_3	1006	890
TiO_2	703	872
SiC	990	1356
Diamond	1840*	1824

*High temperature value ($T \approx \theta_D/2$). Low temperature value is 2230 K.

The same formula can be applied to the insulating compounds considered in this work, but with the anion–cation reduced mass substituted in the formula for the atomic mass. The results are displayed in Table VII, and once again there is a good correlation between the calculated and experimental values, considering the fact that a 20% or more variation in the Debye temperature is not unusual. The experimental values are generally from specific heat or elastic constant data extrapolated to 0 K, although the high temperature value for diamond was used since it appeared to be more appropriate for the thermal expansion calculations. The agreement for the high temperature insulators is about as good as for the alkali halides, indicating that the Morse potential parameters used for these materials are reasonably accurate.

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