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Empirical determination of thermal expansion in insulators with no experimental input

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The localized-continuum model of thermal expansion which was applied to insulators in the previous paper is further refined by empirical means to allow the calculation of thermal expansion in insulating materials with no input other than the chemical formula. Estimation of the Madelung constants is made by using the empirical methods of Kapustinsky and Templeton while the atomic nearest-neighbour distances are estimated by using atomic radii tables. Approximate values of repulsive exponents are obtained by using an empirical scaling rule and a table of monovalent repulsive exponents. The Debye temperature is approximated by a simple formula involving the estimated parameters of the interatomic potential. Using this approach, thermal expansion is estimated in a group of binary and complex ternary materials and a group of complex salts. The agreement with experiment is generally good, although the elimination of experimental input appears to increase the probable error in the calculations by 15% to 20%. The results indicate that this approach is capable of predicting with reasonable accuracy the thermal expansion in a wide range of insulating materials with no experimental input and no adjustable parameters. The limitations of this method for certain cases is also discussed.

1. Introduction

Because such a wide variety of insulating and ceramic materials have been and potentially could be fabricated in the laboratory, it would be quite desirable to be able to estimate, in advance, the various physical properties of each compound. This is particularly true of the thermal expansion, which is one of the most basic properties of materials. Ideally, such an estimation procedure should require no knowledge of other properties of the material in question, since these may be no better known than the thermal expansion, itself.

In the previous paper [1], a localized-continuum model of thermal expansion was presented which showed promise as a means of calculating the thermal expansion of a wide range of insulating materials. The method as it was presented, however, required the knowledge of some experimental properties, principally the detailed crystal structure, the volume compressibility, and the Debye temperature. In this paper, this model will be explored further, to further test its range of applicability, and to further refine its requirements so that no experimental input is necessary. The second requirement is in many cases a necessary prelude to pursuing the first, since in most materials, at least some of the experimental data needed are unavailable. An empirical procedure will be presented for estimating each of the previously required experimental quantities, and the average thermal expansion for both binary and complex materials will be estimated by this approach. As we will see, the relative accuracy of this method suggests it has general applicability for a wide range of materials.

2. Empirical determination of experimental quantities

The experimentally determined quantities which were required in the previous paper for calculating the thermal expansion were the detailed crystal structure, the volume compressibility, and the Debye temperature. In this section, we set forth empirical procedures for determining the required quantities without recourse to experimental information. Basically the approach to be used is as

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follows. The crystal structure was necessary to determine the Madelung constant and the atomic nearest-neighbour distance. However, both of these quantities can be estimated with some accuracy without knowledge of the crystal structure. The volume compressibility was needed to determine the repulsive exponent, but this quantity can be estimated directly by empirical means. Finally the Debye temperature can be approximated by a simple formula involving the parameters of the potential well estimated from the above procedures. We will now discuss each of these procedures in some detail.

2.1. Estimation of the Madelung constant

As is well known, calculation of the Madelung constant requires a mathematical summation of the Coulomb potentials associated with each atomic position in the crystal lattice. However, Kapustinsky [2] discovered some years ago that a simple empirical formula can be used to predict Madelung constants. The simple relation was subsequently examined in more detail by Templeton [3]. Kapustinsky pointed out that a quantity, which has subsequently been referred to as the reduced Madelung constant, is approximately constant for most crystal structures. This quantity, which we will call M_r, corresponds to the Madelung constant per bond in the crystal and is related to the actual Madelung constant M in a binary material by the relation

$$M_r = 2M(r_n)/z_a z_c n \qquad (1)$$

where z_a and z_c are the anion and cation charge numbers, n is the number of atoms per molecule, and the Madelung constant is expressed in terms of the shortest nearest-neighbour distance. The calculated values of M_r for various crystal structures have been found to range from 1.48 to 1.76. Although Templeton demonstrated that by taking into account local symmetry, the above formula could be modified to predict Madelung constants for many structures to within 1% or so, it is obvious that by taking the mean or median value of M_r of 1.6 or 1.64, the Madelung constant for any reasonable structure can be predicted to within ± 10%, without any knowledge of crystal structure. Templeton generalized the above formula for application to ternary and higher order materials by replacing $z_a z_c n$ in the above formula by the sum of squares of the charge numbers of each atom in the molecule. This formula was found to work with comparable success in higher order compounds.

The nearest-neighbour distance can be estimated to within a few percent by using Slater's atomic radii table [4]. Combining this with the Kapustinsky–Templeton estimate for the Madelung constant, the Madelung energy can be estimated within a maximum error of about 15% without any knowledge of crystal structure.

2.2. Estimation of the repulsive exponent

In the previous paper, a simple scaling rule was introduced to estimate repulsive exponents which agreed well with available experimental results. Given the monovalent repulsive exponents m_1 for the alkali halides, the corresponding repulsive exponent for a multivalent compound having average valence Q is given by the relation

$$m_Q - 1 = (m_1 - 1)/Q \qquad (2)$$

It is a simple matter to extend this idea to all atoms of the periodic table by setting the monovalent exponents for any cation–anion pair (or atomic pair) equal to the corresponding exponent for the alkali halide associated with the same two rows of the periodic table. The actual exponent is then determined from the above scaling rule. For example, the value of m_1 for MgO is the same as that for NaF, while the actual repulsive exponent for MgO is determined from the scaling rule to be $(m_{\text{MgO}} - 1) = (m_{\text{NaF}} - 1)/2$. This simple procedure has several advantages. First, it is easy to apply to all atomic pairs. Second, it accounts for the observed tendency of cations in the *b* groups of the period table to have higher values of exponents than cations in the *a* groups having similar ionic radii. For example, Cu^+ has the same ionic radius as Na^+, but is generally associated with a higher repulsive exponent.

Table I lists the monovalent repulsive exponents for each pairwise combination of rows of the periodic table. Most of the values were taken from the experimental determinations of Slater [5] for the alkali halides. The rest were either interpolated from these values or determined from the Born–Mayer formula for the repulsive energy. In the Born–Mayer formulation of the repulsive energy, the quantity r_n/ρ appears rather than the repulsive exponent m, where r_n is again the nearest-neighbour distance and ρ was found to be nearly constant for the alkali halides and equal to 0.345×10^{-8} cm. This formula yields values which agree well with

TABLE I Effective monovalent repulsive exponents for nearest-neighbour atomic pairs

Periods*	m_1	Periods*	m_1
II – II	5.9	V – II	8.4†
II – III	8.0	V – III	9.9†
II – IV	8.7	V – IV	10.0
II – V	9.2†	V – V	11.0
III – II	7.4†	VI – II	8.7‡
III – III	9.1	VI – III	10.3‡
III – IV	9.5	VI – IV	10.8‡
III – V	10.0†	VI – V	11.5‡
IV – II	7.9	VII – II	8.9‡
IV – III	9.7	VII – III	10.5‡
IV – IV	10.0	VII – IV	11.0‡
IV – V	10.5	VII – V	11.6‡

*The first roman numeral refers to the period (row) for the atoms on the left side of the periodic table, the second to that of the atoms on the right side of the periodic table.

†interpolated from Slater exponents for the alkali halides.

‡calculated from $m = r_n/\rho$.

the Slater repulsive exponents when the cations are large, insuring good cation–anion contact. For this reason, the values in the table for the largest cations were obtained from this formula. In the case of the smaller cations where the nearest-neighbour distance is less reliably associated with firm anion–cation contact, the interpolated values were considered more reliable. The repulsive exponents obtained from this table generally agree fairly well with those obtained from available experimental compressibilities.

2.3. Estimation of the Debye temperature

In the previous paper, a simple formula for the cutoff frequency in a linear atomic chain was compared with the experimental Debye temperatures for various materials as a check on the potential well parameters used in the thermal expansion calculations. The formula was found to agree reasonably well with the experimental Debye temperatures in those materials where it is available. This process can obviously be reversed and the approximate formula used to estimate the Debye temperatures for the large number of materials where no experimental values are available. The approximate formula

$$\bar{\theta}_D = (2\hbar/k)a(2D/\mu)^{1/2} \tag{3}$$

involves only the two parameters of the Morse potential, which can be obtained from the above empirical procedures, and the anion–cation reduced mass μ. Consequently, θ_D can be estimated from this formula with no knowledge other than the chemical formula of the compound. In

TABLE II Calculated versus experimental thermal expansion coefficients for various binary compounds

	Q	$\bar{\theta}_D$(K)	T(K)	α_{calc}($\times 10^6$ K^{-1})	α_{exp}($\times 10^6$ K^{-1})
BeO*	2	1461	293	5.5	6.3
			1600	14.7	12.8
CaO	2	543	293	14.5	11.2
			1000	17.5	13.6
UP	3	410	293	8.3	7.8
			1000	9.3	9.6
UN	3	663	293	7.0	7.4
			1000	8.9	10.4
US	2	335	293	15.0	11.1
			1000	16.5	12.9
BN	3	1587	293	2.4	1.8
			1000	6.7	5.9
BP	3	1187	293	3.7	2.9
			1000	7.0	5.4
WC*	4	1042	293	2.9	3.7
			1000	4.9	5.1
TiN	3	867	293	5.6	6.3
			1000	8.1	10.0

*polycrystalline samples.

most cases, the formula gives a value which is within 20% of the experimental Debye temperature when it is available for comparison.

3. Calculation of thermal expansion in simple binary compounds

Using the above empirical procedures, it is a straightforward calculation to determine the thermal expansion coefficients of simple binary compounds. In the Kapustinsky Equation 1, M_r is set equal to 1.64 in all cases to give a maximum error in the Madelung constant of about 10%, regardless of crystal structure. Using Equations 1, 2 along with Table I, and Equation 3 in conjunction with the equations of the previous paper, the thermal expansion coefficients of a group of binary compounds have been determined, with the results listed in Table II. Listed in the table are the values of Q which are used in Equation 2 in conjunction with Table I for determining the repulsive exponents, the estimated Debye temperatures as determined from Equation 3, and the calculated and observed coefficients of thermal expansion at room temperature and an elevated temperature which is a large fraction of the melting temperature for each compound. The observed coefficients of thermal expansion were taken from the compilation of Touloukian *et al.* [6].

The probable error in the calculations appears to be about 25%, which is between 15% to 20% higher than the probable error in the calculations in the previous paper which used experimental information. This is about the penalty which is to be expected in using the estimation methods discussed above rather than experimentally determined quantities. Considering, however, the fact that the calculated values are arrived at with no experimental input and no adjustable parameters, the probable error is quite reasonable. The relative errors in the calculated values at the two temperatures is a measure of the accuracy of the calculated Debye temperature. A significant difference in the percentage errors for the two temperatures is an indication of a significant error in $\bar{\theta}_D$. The tabulated results appear to indicate that the values of $\bar{\theta}_D$ are reasonably accurate in all cases. Since an average thermal expansion is being calculated here, the values of α for polycrystalline samples of the noncubic crystals are compared with the calculated values. As was found in the previous paper, crystal anisotropy does not appear to significantly diminish the agreement between calculated and observed values.

4. Calculation of thermal expansion in higher order compounds

The relative success of the calculation for the binary materials suggests that this procedure should also work well for higher order compounds. The procedure is applicable to higher order compounds with only minor modifications. First, the Templeton generalization of the Kapustinsky formula for the Madelung constant must be used. If M_r is set equal to 1.6 in all cases, the Templeton–Kapustinsky Madelung constant is given by

$$M(r_n) = 0.8 \sum_i z_i^2 \tag{4}$$

for all crystal structures. There is insufficient information at present to know whether this formula will be accurate to ± 10% for all possible complex structures. However, comparisons made so far appear to indicate that Equation 4 has an accuracy for complex compounds comparable to that of Equation 1 for the binary compounds. The sum in Equation 4 is generally made over all atoms in the simplest chemical formula. Therefore, the use of Equation 4 in the Madelung energy does not require as a factor either the number of atoms per molecule or the least common divisor of the atomic valences.

Since the use of Equation 4 involves a sum over all atoms in the molecular group, the nearest-neighbour distance in the Madelung energy must be replaced by a weighted average nearest-neighbour distance. Similarly, a weighted average repulsive exponent must be computed. The procedure discussed above for binary compounds is repeated for each possible nearest-neighbour atomic pair, and the average is calculated by weighting the result for each pair according to its frequency in the chemical formula. Finally, the binary reduced mass in Equation 3 is replaced by a weighted average nearest-neighbour reduced mass.

This procedure has been applied to a calculation of the thermal expansion coefficients in a group of complex oxides and the results are listed in Table III. In this case, the effective repulsive exponent m_Q is listed rather than Q, and the experimental thermal expansion coefficients were once again taken from reference [6]. The calculated and observed values agree about as well as did the values for the binary materials. This

TABLE III Caluculated versus experimental thermal expansion coefficients for some complex oxide compounds

	m_Q	$\bar{\theta}_D$(K)	T(K)	α_{calc}($\times 10^6$ K^{-1})	α_{exp}($\times 10^6$ K^{-1})
$BaTi_4O_9$	3.8	766	293	6.9	7.4
			1000	9.3	10.0
$Ca_3Al_2O_6$	4.1	685	293	10.5	6.8
			1000	13.6	11.6
$CaAl_2O_4$	3.9	782	293	8.6	4.7
			1000	11.9	7.8
$MgAl_2O_4$	3.8	845	293	7.9	7.0
			1000	11.5	9.8
Mg_2SiO_4	3.9	870	293	7.4	9.0
			1000	10.8	12.8
$MgSiO_3$	3.7	945	293	6.1	8.6
			1000	9.5	13.9
$BaTiO_3$*	4.1	647	293	8.8	6.3
			1000	11.1	14.7
$SrTiO_3$	4.0	670	293	8.6	10.3
			1000	11.1	12.0
Al_2TiO_5*	3.6	882	293	6.4	8.1
			1000	9.6	9.7

*polycrystalline samples.

implies that the generalization of the estimation procedures to higher order compounds is about as accurate as are the procedures for the binary compounds. A particularly interesting result is that for Al_2TiO_5 which is a highly anisotropic crystal. In spite of this, the calculated average coefficient of thermal expansion agrees well with the observed value for polycrystalline samples, indicating once again that crystalline anisotropy does not significantly affect the accuracy of the calculation. These results indicate this procedure is applicable to a wide range of insulating compounds having almost any degree of molecular and/or crystalline complexity.

5. Calculation of thermal expansion in complex salts

Complex salts represent another category of insulating material whose thermal expansion can be estimated rather effectively by a modification of this technique. A complex salt is composed of a positively charged cation and a complex molecular radical having a negative charge. Since dissociation normally takes place between the two charged entities, most of the thermal expansion involves the vibration between them. Because the thermal expansion in these materials can be so large and is potentially so variable, they are particularly interesting materials to apply this procedure to.

The simplest way to estimate the thermal expansion in these materials is to ignore the internal vibrational effects in the complex radical and attribute the thermal expansion solely to the interionic vibrations. The complex radical is then looked upon as a large, massive, negatively charged ion. Although one could estimate the size of the complex radical by purely geometric means using atomic radii tables, for illustrative purposes, we will use the idea of the thermochemical radius reviewed in detail by Waddington [7]. The basic idea here is that if the dissociation energy of a binary complex salt in which the chemical formula includes one cation and one complex radical is known from experimental determination, then the thermochemical radius of the complex radical can be deduced using the Goldschmidt ionic radius for the cation and the Born–Mayer energy formula for the alkali halides. Thus, the Coulomb energy and the repulsive energy, and from this the repulsive exponent, can be immediately deduced. The thermochemical radii for a large number of complex radicals have been obtained in this way and are listed by Waddington.

Table IV lists the results of calculations on

TABLE IV Calculated versus experimental thermal expansion coefficients for some complex salts

	m_Q	$\bar{\theta}_D$(K)	T(K)	α_{calc}($\times 10^6$ K^{-1})	α_{exp}($\times 10^6$ K^{-1})
$NaClO_3$	8.6	246	293	52.1	43.0
			500	55.8	59.8
$NaBrO_3$	8.4	243	293	51.6	37.6
			500	55.1	45.9
$NaIO_4$ *	10.1	207	293	54.1	37
			450	57.2	52
$NaNO_3$ *	8.3	262	293	51.7	40
			450	54.8	67
$CaCO_3$ *	8.4	433	293	11.4	4.0
			700	12.8	8.6
$MnCO_3$ *	7.8	423	293	11.2	9.3
			500	12.1	10.9

*polycrystalline samples.

some of these compounds using this method. The experimental values were once again taken from reference [6]. As can be seen from the results, the high temperature coefficients calculated by this procedure are fairly accurate, lending some support to the approximation that the thermal expansion arises primarily from the interionic vibrations in these materials. However, the room temperature results are in considerably poorer agreement with experiment. This is due to the fact that the calculated Debye temperatures are generally too low. Although this is partly a result of not including the internal vibrational degrees of freedom in the calculation which would of course contribute to the Debye temperature, the primary reason for the discrepancy is the treatment of the negatively charged radical as a massive ion, which leads to a significant underestimation of the Debye temperature. A better approximation might be to take the average reduced mass of the atoms in the complex radical rather than the reduced mass associated with the massive whole. Aside from this deficiency, these calculations appear to agree with experiment about as well as the previous ones, indicating that this approach is capable of handling a wide range of material types and magnitudes of the thermal expansion coefficient, since the coefficients for some of these compounds are in some cases two orders of magnitude higher than for many high temperature compounds. Also, as was the case in previous calculations, the accuracy does not appear to have been effected by sometimes large crystalline anisotropies.

6. Limitations to the model

The localized-continuum model of thermal expansion, which was presented in the previous paper and further refined in this one, appears capable, based on experience so far, of predicting thermal expansion with reasonable accuracy in about 90% of insulating materials. In the other 10% of the cases, the errors may approach 100%, and there appears to be two different reasons for this. In most of these anomalous cases, an unusual local symmetry or coordination number often brings about a significant change in the thermal expansion. Slack [8] has obtained considerable empirical evidence that anomalous coordination numbers in complex crystal structures can be correlated with anomalous thermal expansion coefficients. Clearly, a model which uses only the chemical formula cannot account for these anomalies. However, a modification of the procedure based on local coordination numbers in the absence of experimentally determined compressibilities is certainly feasible. Since the repulsive exponents are estimated for "normal" coordination numbers associated with a given valence, modified exponents associated with unusual coordination numbers can easily be determined. Such modifications appear to account for the thermal expansion anomalies in the few cases where detailed structural information is available.

In a few percent of the cases encountered, anomalous temperature dependence of the thermal expansion results from the behaviour of one or more normal modes which produce a contraction in the material with rising temperature. This happens rather dramatically, for example, in ZnS and CdS, where at low temperatures, the coefficient of thermal expansion is strongly negative. As a result, this model predicts a much higher coefficient than is observed, since the calculated coefficient is a monotonically increasing function of temperature. Negative thermal expansion is commonly observed in solids with open structures, particularly those which have small values of one or more of the shear moduli. It is generally believed to arise from a relatively high density of transverse modes of vibration which are possible in such open structures. Such normal modes, by counteracting the effects of all the others, can produce in some extreme cases a very low thermal expansion over extended temperature ranges. This model in its present form cannot account for such behaviour without modification. Accounting for this type of behaviour requires that the properties of such normal modes be specifically incorporated in the model of thermal expansion. Interestingly, however, the model used in this paper, which gives what might be called an "average" or "expected" thermal expansion for a given material, can usually pinpoint the nature of such anomalies by examining the temperature dependence of the difference between the calculated and observed thermal expansion coefficients.

7. Conclusions

The calculations presented in this paper have demonstrated that the localized-continuum model of thermal expansion, which was initially applied to insulators in the previous paper, is capable with various empirical techniques of predicting with reasonable accuracy the thermal expansion in a wide variety of insulating materials with no experimental input and no adjustable parameters. In the 10% or so of the cases where the expansion predicted by the model are in poor agreement with experimental, structural or normal mode anomalies usually exist whose nature can usually be elucidated by comparing the predicted results with experiment.

Although the theory is based upon an idealized Morse interatomic potential, its connection with real materials is based upon a series of empirical rules based in turn upon a potential function associated with the ionic model. Since this approach appears to work well regardless of bond type, the basic theoretical question of why the bottom of the thermal potential in solids is largely independent of bond type remains to be answered.

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