

Computer Simulation of Thermal Expansion of Non-Cubic Crystals: Forsterite, Anhydrite and Scheelite

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(Received 1 April 1975; accepted 26 June 1975)

The thermal expansion of non-cubic crystal structures may be simulated by a geometric least-squares refinement of the known structure after predicting the thermal expansions of various coordination polyhedra. This method has been applied to forsterite, Mg_2SiO_4 , anhydrite, $CaSO_4$, and scheelite, $CaWO_4$. The expansions of different M–O bonds (M = Mg or Ca) are predicted by using an empirical relationship between the expansion coefficient, α , and bond-strength, s . The expansions of the polyhedral edges are approximated from the changes in the average M–O bond lengths. The rigid tetrahedral groups (SiO_4 , SO_4 or WO_4) were assumed to retain their size and shape during the process of thermal expansion. The structural changes are simulated at 300°C for forsterite and at 200°C for anhydrite and scheelite. Calculated changes in the position parameters for forsterite are generally in the same direction as those observed experimentally. The lattice parameters compare well and calculated values of the expansion coefficients along the three crystallographic axes show the same trend as the observed values namely $\alpha_a < \alpha_c < \alpha_b$. Thermal expansion behavior of anhydrite has been determined experimentally in the temperature range 20–275°C and the structure has been simulated at 200°C. The observed and calculated values of the expansion coefficients agree well; both show that $\alpha_a > \alpha_c \gg \alpha_b$. The calculations on scheelite successfully reveal the characteristic anisotropic thermal expansion behavior of scheelite-type structures, which is $\alpha_a < \alpha_c$.

Introduction

Thermal expansion is a structure-dependent physical property of a crystalline solid, but the attempts to predict the expansion behavior of a known crystal structure have met with limited success. Theoretical evaluation of the coefficient of expansion is possible if the effective potential well in which a particular atom is situated is known [see for example, Smyth (1955), Mitra & Joshi (1961) and Killean (1974)]. However, this method is only suitable for calculating the average expansion coefficient of simple metals and ionic crystals where the displacements of the atoms are controlled by a single force constant. It is attempted here to predict the anisotropic thermal-expansion behavior of some simple ionic solids from their crystal structures. The approach is empirical and the method essentially consists of calculating the unit-cell and position parameters of a structure after predicting the expansion of various coordination polyhedra. Because of the moderate complexity of their structures forsterite, Mg_2SiO_4 , anhydrite, $CaSO_4$, and scheelite, $CaWO_4$, are selected to outline the method and to analyze the results.

Procedure

An ionic structure may be visualized as a system of coordination polyhedra. As suggested earlier (Khan & Baur, 1973), rigid tetrahedral groups may not change size significantly during the process of thermal expansion. The reported high-temperature studies on several silicates show that the Si–O bonds have a

negligibly small expansion coefficient at moderately high temperatures (Brown & Prewitt, 1973; Cameron, Sueno, Prewitt & Papike, 1973; Smyth, 1973; Sueno, Cameron, Papike & Prewitt, 1973). Similarly, the high-temperature work on some tetragonal KH_2PO_4 -type crystals reveals that the PO_4 and AsO_4 groups do not expand much upon heating (Khan, unpublished). It was assumed here, accordingly, that the T–O bonds (T = Si, S or W) do not change lengths during the thermal expansion of the lattice. This assumption deliberately ignores the experimental results of Smyth & Hazen (1973) which show that in forsterite three of the four Si–O bonds of the silicate group contract significantly upon heating from room temperature to 300°C [see Table 1]. The lattice expansion in these structures is thus attributed to the expansion of Mg–O or Ca–O bonds. It is further assumed that the various M–O bonds (M = Mg or Ca) within a coordination polyhedron expand according to their electrostatic bond strengths (s). For simple ionic structures Megaw (1939) has reported an empirical rule, $\alpha_{av} \times (Z/C.N.)^2 \times 10^6 = 1$, where α_{av} is the average linear expansion coefficient and Z and $C.N.$ are respectively the valency and coordination number of an ion; $(Z/C.N.)$ actually represents the electrostatic bond-strength (s). A somewhat similar relationship is observed in some recently investigated pyroxenes. Cameron, Sueno, Prewitt & Papike (1973), have evaluated the mean expansion coefficients of various types of atomic bonds in several isomorphous clinopyroxenes after the structural studies of the series at various temperatures. Fig. 1 is a graphical representation of the variation of α_{av} and

s_{av}^2 for these bonds; α_{av} and s_{av} respectively represent the average expansion coefficient and average bond-strength. The bond strength of various M-O bonds in a structure can be calculated using the procedure and constants given by Brown & Shannon (1973). The empirical curve (Fig. 1) was used to estimate the expansion coefficients of various bonds and the bond lengths were calculated at a desired temperature. The O-O edges of the tetrahedral groups were generally assumed to remain unchanged. The changes in the O-O lengths around the M ions were estimated as follows: All the O-O lengths (less than 3.5 Å) and the corresponding O-M-O angles were averaged and the 'average' M-O length was calculated. Its expansion for the desired interval of temperature was estimated using the procedure described above. With the new M-O length and the average O-M-O angle the change, $\Delta(O-O)$, in the average O-O length was calculated. The new O-O lengths were determined by adding $\Delta(O-O)$ to their initial lengths.

A least-squares program (*DLS*) developed by Meier & Villiger (1969) has been used by Baur (1972) for the simulation of crystal structures of the polymorphs of Mg_2SiO_4 . The same program was employed here to simulate the changes in atomic positions and lattice parameters in forsterite, ahnydrite, and scheelite after introducing the predicted interatomic distances at a higher temperature. Because of the small changes involved, the predicted bond lengths must be accurate up to the fourth decimal place. A unit weight was assigned

to the T-O and M-O bonds and the O-O lengths were given a much smaller weight equal to 0.1. This weighting scheme has been adopted after several trials and

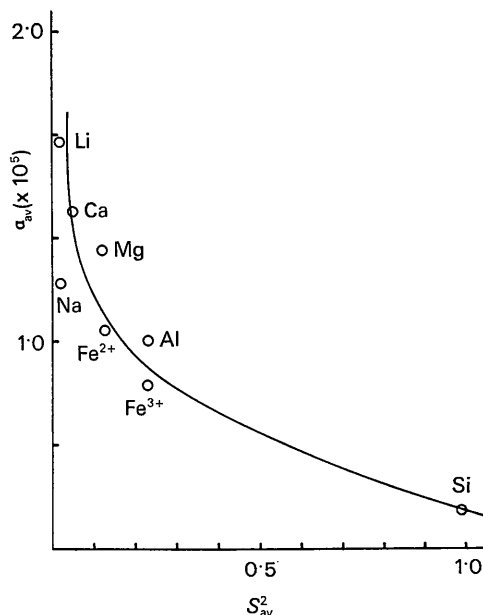


Fig. 1. Average expansion coefficient (α_{av}) of cation-oxygen bond length vs. the square of the bond strength (s_{av}^2), based on the data on seven clinopyroxenes reported by Cameron, Sueno, Prewitt & Papike (1973).

Table 1. Predicted and observed bond lengths in forsterite at different temperatures

s is the bond strength calculated using the procedure and constants given by Brown & Shannon (1973), α is the expansion coefficient estimated from Fig. 1, and W is the weight assigned to the bond in the *DLS* refinement. Observed data from Smyth & Hazen (1973). Also see text.

Bond lengths	at 25°C				Bond lengths at 300°C		Bond lengths at 600°C	
		s^2	α	W	Predicted	Observed	Predicted	Observed
2 × Mg(1)-O(2)	2.068 (1) Å	0.128	1.13	1.00	2.0748 Å	2.080 (3) Å	2.0875 Å	2.085 (3) Å
2 × Mg(1)-O(1)	2.085 (1)	0.118	1.16	1.00	2.0913	2.089 (3)	2.0961	2.099 (3)
2 × Mg(1)-O(3)	2.132 (1)	0.095	1.24	1.00	2.1392	2.140 (3)	2.1477	2.154 (3)
Mg(2)-O(2)	2.051 (2)	0.139	1.08	1.00	2.0574	2.058 (6)	2.0645	2.066 (5)
2 × Mg(2)-O(3)	2.067 (1)	0.129	1.11	1.00	2.0734	2.075 (4)	2.0818	2.080 (3)
Mg(2)-O(1)	2.182 (2)	0.075	1.34	1.00	2.1903	2.196 (6)	2.2052	2.220 (5)
2 × Mg(2)-O(3)	2.214 (1)	0.065	1.42	1.00	2.2232	2.231 (4)	2.2408	2.244 (4)
2 × O(2)-O(1)†	2.847 (3)			0.10	2.8567	2.857 (7)	2.8675	2.870 (6)
2 × O(2)-O(1)	3.023 (1)			0.10	3.0330	3.036 (1)	3.0466	3.045 (1)
2 × O(2)-O(3)	3.336 (2)			0.10	3.3457	3.376 (5)	3.3866	3.396 (5)
2 × O(2)-O(3)*	2.553 (2)			0.10	2.5576	2.532 (6)	2.5374	2.537 (4)
2 × O(1)-O(3)	3.104 (2)			0.10	3.1138	3.110 (5)	3.1204	3.121 (5)
2 × O(1)-O(3)†	2.854 (2)			0.10	2.8639	2.865 (5)	2.8762	2.889 (5)
2 × O(2)-O(3)	2.930 (2)			0.10	2.9405	2.923 (5)	2.9347	2.932 (5)
2 × O(2)-O(3)	3.193 (2)			0.10	3.2028	3.227 (6)	3.2383	3.246 (5)
O(3)-O(3)	3.386 (2)			0.10	3.3962	3.416 (5)	3.4272	3.432 (4)
2 × O(3)-O(1)	3.028 (2)			0.10	3.0383	3.054 (5)	3.0650	3.072 (5)
2 × O(3)-O(3)	2.997 (1)			0.10	3.0070	3.017 (5)	3.0281	3.029 (4)
O(3)-O(3)*	2.594 (2)			0.10	2.5992	2.583 (5)	2.5889	2.585 (4)
Si-O(1)	1.615 (2)			1.00	1.6149	1.620 (5)	1.6197	1.615 (5)
2 × Si-O(3)	1.635 (1)			1.00	1.6353	1.622 (4)	1.6219	1.621 (3)
Si-O(2)	1.653 (2)			1.00	1.6530	1.632 (5)	1.6316	1.636 (5)
2 × O(1)-O(3)	2.757 (2)			0.10	2.7571	2.745 (5)	2.7448	2.739 (5)
O(1)-O(2)	2.743 (3)			0.10	2.7437	2.722 (7)	2.7221	2.719 (6)

* Shared edge between an octahedron and a tetrahedron.

† Shared edge between two octahedra.

errors which included a scheme according to the bond strength, s , and another according to s^2 . The final results were not very different as long as the O–O lengths were assigned a uniform but much smaller weight than the T–O and the M–O bonds. The assignment of widely different weights to the O–O edges, even when these belong to different types of coordination polyhedra, is not recommended. The refinements were considered to have converged when the changes in the lattice parameters were less than 0.001 Å; at that stage the changes in the position parameters were never more than 0.0001.

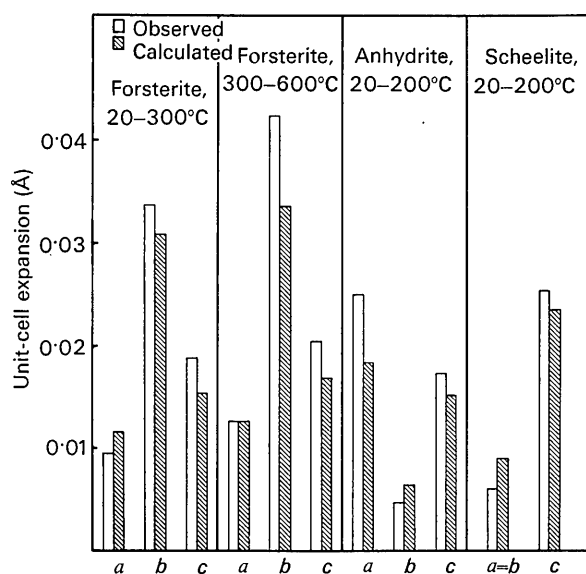


Fig. 2. Observed and calculated thermal expansion of lattice parameters of forsterite, anhydrite, and scheelite for the indicated change in temperature.

Results and discussion

Forsterite

The crystal structure of forsterite, Mg_2SiO_4 , has been studied at room temperature and above (Smyth & Hazen, 1973). The orthorhombic unit cell of forsterite may be visualized as consisting of two crystallographically different MgO_6 octahedra and one silicate tetrahedron per formula unit (four formula units/unit cell). The bond lengths at room temperature are given in Table 1. Of the 12 Mg–O bonds in the two octahedra, seven are crystallographically independent and their lengths fall in a range between 2.051 and 2.216 Å. The square of their bond strengths, s^2 , and the corresponding expansion coefficients, estimated from Fig. 1, are listed respectively in columns 3 and 4 of Table 1. The input to the *DLS* refinements consisted of the atomic positions and lattice parameters reported at 20°C (Smyth & Hazen, 1973), and the predicted distances at 300°C and the assigned weights which are listed respectively in columns 6 and 5 of Table 1. Shared edges were included with average lengths. The same procedure was followed for simulating the structural changes from 300 to 600°C. The input to this refinement was the atomic positions and lattice parameters reported by Smyth & Hazen at 300°C, and the predicted distances at 600°C as listed in Column 8 of Table 1. The calculated and observed shifts in atomic positions are compared in Table 2, the lattice parameters in Table 3 and the observed and calculated changes in the lattice parameters are graphically compared in Fig. 2.

The results obtained here are promising. The anisotropic thermal expansion behavior of the forsterite structure could be predicted with success. The calculated lattice parameters compare well with the observed values at 300°C (Table 3), and the calculated values of the expansion coefficients show the same trend as the

Table 2. Calculated and observed shifts in atomic coordinates ($\times 10^4$) in forsterite upon changing the temperature

	Observed data from Smyth & Hazen (1973).											
	From 25°C to 300°C						From 300°C to 600°C					
	Δx		Δy		Δz		Δx		Δy		Δz	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Mg(1)	0	0	0	0	0	0	0	0	0	0	0	0
Mg(2)	-4	0 (5)	1	6 (2)	0	0	-5	4 (5)	1	5 (2)	0	0
Si	2	-5 (4)	-3	-1 (2)	0	0	2	0 (3)	-3	2 (2)	0	0
O(1)	-6	0 (10)	-1	-3 (3)	0	0	-7	-20 (9)	-1	-4 (4)	0	0
O(2)	-5	-38 (10)	2	18 (5)	0	0	-6	1 (9)	2	5 (4)	0	0
O(3)	8	29 (7)	-2	-9 (3)	7	16 (6)	9	16 (6)	-2	0 (3)	7	5 (5)

Table 3. Calculated and observed lattice parameters of forsterite at different temperatures

	Observed data from Smyth & Hazen (1973).					
	25°C	300°C		600°C		
		Calc.	Obs.	Calc.	Obs.	
a	4.756 (5) Å	4.767 Å	4.763 (5) Å	4.7757 Å	4.778 (5) Å	
b	10.207 (10)	10.2378	10.240 (10)	10.2736	10.290 (10)	
c	5.980 (6)	5.9955	5.999 (6)	6.0159	6.017 (6)	

experimentally observed values namely $\alpha_a < \alpha_c < \alpha_b$ (Table 4). This agreement is quite surprising in view of the differences which exist in the observed and predicted bond-lengths (Table 1), particularly in the Si–O distances at 300°C. The Si–O bond lengths are experimentally found to change from (1.615, 2×1.635 , 1.653 Å) at room temperature to (1.620, 2×1.622 , 1.632 Å) at 300°C. The simulated structure, on the other hand, requires no change in the Si–O distances upon heating. The agreement between the calculated and observed shifts in the atomic positions is poor (Table 2). It may be pointed out, however, that the calculated and observed shifts have the same signs for significantly large values of the observed shifts. That the calculated shifts are following the observed values is even more obvious if the calculated shifts between 20° and 300°C and between 300° and 600°C are added and compared with the observed shifts. In this way the simulated structure tends to be similar to the observed structure, but more so in the unit-cell dimensions than in the atomic coordinates. It must also be recognized in this connection that the simulated structure depends entirely on geometrical considerations and does not account for any apparent shifts in the atomic positions due to thermal motions. It is likely that the observed contraction of the Si–O bond lengths in forsterite, upon heating from room temperature to 300°C, is a manifestation of a newly excited mode of vibrations.

The simulated results from 300°C to 600°C indicate that the procedure is not very sensitive for predicting the temperature variations of the expansion coefficients. The calculated changes in the parameters, for the range 300–600°C are essentially the same as from room temperature to 300°C (Tables 2 and 3 and Fig. 2). This observation is quite interesting because for the SiO₄ groups the predicted and observed distances, unlike at 300°C, are much closer at 600°C. It appears that the method has an averaging effect which makes the calculated value of the larger expansion coefficient slightly smaller than the observed. Perhaps a modified form of the curve shown in Fig. 1 will improve the situation. The present procedure is, nevertheless, useful in predicting the expansion behavior in a higher temperature range also. The agreement between the cal-

culated and observed values is quite good for the *a* and *c* axes. The difference in the two values for the *b* axis is also not very significant, when it is considered that this parameter has the largest experimental error. The agreement between the calculated and observed values of the average expansion coefficient, α_{av} , may be considered good for the range 20–300°C and as well as the higher temperature range (Table 4).

Anhydrite, CaSO₄

The crystal structure of anhydrite has been refined at room temperature by Höhne (1963). Since there is no high-temperature data available in literature for this mineral, temperature variations of lattice parameters were determined at different temperatures. A crystal of anhydrite, sealed in a quartz capillary, was mounted on an automatic diffractometer equipped with a high-temperature furnace. The furnace is similar to the one described by Brown, Sueno & Prewitt (1973) and the details of the calibration will be described elsewhere. Lattice parameters were determined at three different temperatures, between 20 and 275°C, using twelve carefully centered reflections. The results are graphically shown in Fig. 3. The lattice parameters at 20°C [*a* = 6.243 (4), *b* = 7.005 (4) and *c* = 6.987 (5) Å] compare better with the values reported by Swanson, Fuyat & Ugrinic (1955) at room temperature as (*a* = 6.238, *b* = 6.996 and *c* = 6.991 Å) than with the values reported by Höhne (1963) (see Table 5). Since the present values were determined from the reflections with small *2θ* values (around 35°), it is likely that these are affected by systematic errors. However, the same set of reflections was used at three different temperatures and therefore the changes in the lattice parameters and the evaluated values of the expansion coefficients must be reliable.

The crystal structure of anhydrite was simulated at 200°C, starting with the structure reported by Höhne (1963). The Ca atoms are coordinated by eight oxygen atoms which form two interpenetrating disphenoids. Two edges of this CaO₈ polyhedron are shared with the neighboring SO₄ tetrahedra. The eight Ca–O bond lengths are (2×2.324 , 2×2.427 , 2×2.579 Å) and the S–O bond lengths are (2×1.467 and 2×1.480 Å). By

Table 4. *Calculated and observed expansion coefficients ($\times 10^6$) along a, b and c axes in forsterite, anhydrite and scheelite*

α_{av} represents the average linear expansion coefficient.

	Forsterite from 20°C to 300°C			Forsterite from 300°C to 600°C			Anhydrite from 20°C to 200°C		Scheelite from 20°C to 200°C	
	Calc.	Obs.		Calc.	Obs.		Calc.	Obs.	Calc.	Obs.*
	Skinner (1962)	Smyth & Hazen (1973)		Skinner (1962)	Smyth & Hazen (1973)				Deshpande & Suryanarayana (1969)	
α_a	8.7	8.8	5.4	8.9	9.7	8.1	16.4	22.2	9.5	6.4
α_b	10.8	11.8	11.8	10.9	13.4	14.1	5.1	3.3	—	—
α_c	9.3	10.7	11.6	9.4	11.9	10.8	12.1	13.9	11.5	12.4
α_{av}	9.6	10.4	9.6	9.7	11.7	11.0	11.2	13.1	10.2	8.4

* At room temperature

following the procedure described above, the structural parameters were calculated at 200°C. The agreement between calculated and observed changes in the lattice parameters improved slightly when the shared edges between the rigid SO₄ groups and CaO₈ poly-

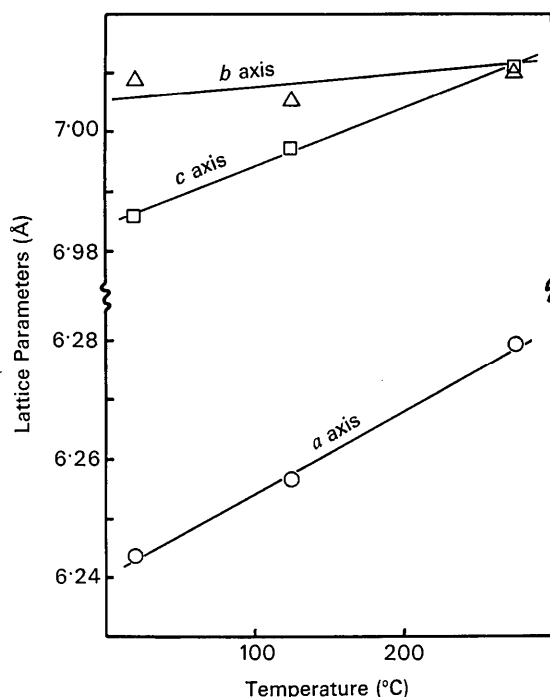


Fig. 3. Temperature variation of the lattice parameters of anhydrite, CaSO₄. Experimental data.

hedra were assumed to remain unchanged during the expansion of the structure. The initial and final structural parameters are compared in Table 5, the observed and calculated expansion of the unit-cell are compared in Fig. 2 and the expansion coefficients are compared in Table 4. The simulated expansion behavior of anhydrite compares well with the observed data. The observed and calculated expansion coefficients show the same trend $\alpha_a > \alpha_c \gg \alpha_b$, and the corresponding values are comparable. As in the case of forsterite, the calculated values of the larger expansion coefficients are somewhat smaller than the observed. The observed and calculated results indicate that the orthorhombic unit cell of anhydrite becomes pseudo-tetragonal around 300°C.

Scheelite, CaWO₄

The crystal structure of scheelite has been accurately determined at room temperature by Zalkin & Templeton (1964). The expansion coefficients α_a and α_c of the tetragonal unit cell at room temperature are reported by Deshpande & Suryanarayana (1969). The Ca atoms have a coordination similar to that in anhydrite and the eight Ca–O bond lengths are (4×2.436 and 4×2.481 Å). The four W–O bonds in the WO₄ tetrahedron are identical and equal to 1.785 Å. The structure was simulated at 200°C. The initial and final structural parameters are given in Table 6, the observed and calculated expansion of *a* and *c* axes are compared in Fig. 2, and the expansion coefficients are compared in Table 4. The calculated results indicate that $\alpha_a = \alpha_b < \alpha_c$. The experimental results (Deshpande & Suryanarayana, 1969) show that this type of anisotropy is characteristic of scheelite-type structures.

Table 5. Structural parameters of anhydrite, CaSO₄, as observed at room temperature and calculated at 200°C

Space group: *Bbmm*.

Lattice parameters	Observed at 20°C (Höhne, 1961)			Calculated at 200°C		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
	6.23 Å	6.98 Å	6.97 Å	6.2484 Å	6.9864 Å	6.9852 Å
Position parameters	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Ca	0.346	0.75	0.0	0.3458	0.75	0.0
S	0.154	0.25	0.0	0.1539	0.25	0.0
O(1)	0.296	0.080	0.0	0.2958	0.0804	0.0
O(2)	0.020	0.25	0.173	0.0206	0.25	0.1728

Table 6. Structural parameters of scheelite, CaWO₄, as observed at room temperature and calculated at 200°C

Space group: *I4₁/a*.

Lattice parameters	Observed at 20°C (Zalkin & Templeton, 1964)			Calculated at 200°C		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
	5.243 (2) Å		11.376 (3) Å	5.2520 Å		11.3996 Å
Position parameters	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Ca	0.0	0.25	0.625	0.0	0.25	0.625
W	0.0	0.25	0.125	0.0	0.25	0.125
O	0.1504	0.0085	0.2110	0.1499	0.0088	0.2108

Conclusion

The procedure described in this paper has been successful in predicting the anisotropic thermal expansion behavior of three ionic structures, forsterite, Mg_2SiO_4 , anhydrite, $CaSO_4$, and scheelite, $CaWO_4$. The agreement between the observed and calculated values of the average linear expansion coefficient is also good. These results indicate that the procedure is at least useful for predicting the thermal-expansion behavior of simple structures. The method appears to have an averaging effect, making the calculated values of the larger expansion coefficients somewhat smaller than the observed. It is felt that a properly modified form of the relation between the bond strength, s , and the expansion coefficient, α , will improve the agreement. Perhaps a smaller interval of temperature will also help. The results may also improve by developing a procedure to take the anion-anion and cation-cation interactions into account. It has been pointed out that the anion-anion repulsions influence the expansion coefficients of halite-type alkali halides (Khan, 1974). Predicting the expansion of the O-O edges of the polyhedra, particularly the shared ones, is rather arbitrary. It is hoped that experience with a few more structures will help resolve some of these problems. In well refined structures, it will be tempting to explore the possibility of improving the accuracy of the predicted bond lengths by using the information regarding the thermal ellipsoids of atoms.

The three structures used here have a common feature; rigid tetrahedral groups joined by relatively weak Mg-O and Ca-O bonds. In order to fully determine the usefulness and limitations of this technique it will be necessary to apply it to several other solids including simple oxides and the structures containing anionic groups other than isolated tetrahedra. An attempt to predict the negative expansion of calcite in the plane normal to the c axis was not successful. The higher symmetry of calcite reduces the number of crystallographically different bond lengths in the structure and the input to the DLS refinement is limited. A

knowledge of detailed dynamical behavior may be necessary for simulating the unusual expansion behavior of such a structure.

I thank Dr E. Olsen of the Field Museum of Natural History for the loan of a specimen of anhydrite. Computer time provided by the Computer Center of the University of Illinois at Chicago Circle is gratefully acknowledged.

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