Lattice-dynamical evaluation of atomic displacement parameters of minerals and its implications: The example of diopside

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ABSTRACT

A Born–von Kármán rigid-ion, lattice-dynamical model has been applied to diopside with the use of empirical potentials derived by fitting the vibrational frequencies of a group of nesosilicates and oxides (including quartz). The Raman and infrared spectra are satisfactorily interpreted by these calculations; there is also good agreement with anisotropic atomic displacement parameters (ADPs) derived from accurate crystal-structure refinement at various temperatures. The agreement with theoretical and experimental data of independent origin confirms the physical meaning of both experimental and calculated ADPs; consequently, the correlation tensors between the displacement of different atoms, which can be evaluated in this way and cannot be obtained from Bragg diffraction measurements, are also reliable, thereby allowing bond-length correction for libration in the most general case. As for other oxides and silicates, the zero-point motion contribution amounts to about 35% of the total at room temperature. Hirshfeld's rigid-bond test applied to the SiO_4 groups is in agreement with our calculations. The values of thermodynamic functions such as the specific heat and entropy at different temperatures are also satisfactorily reproduced, although a rigid-ion model has been used and the empirical potentials were not specifically fitted to the properties of the substance under study: For this purpose, a simple treatment of anharmonic expansion is proposed. Therefore, the possibility of transferring empirical potentials to widely different groups of minerals and that of developing a routine application to derive accurate values for various properties of pure minerals at various temperatures, starting only from crystal data, are confirmed.

INTRODUCTION

Anisotropic atomic displacement parameters (ADPs), as components of second-rank tensors $U_k = \langle u_k u_k^T \rangle$, where u_k is the displacement column vector relative to the atom k (and u_k^T is its transpose), have been commonly used in crystal-structure refinement for nearly 40 years. Cruickshank (1956a) included these tensors, which are consistent with harmonic lattice dynamics (Willis and Pryor 1975), in the now classic expressions for temperature factors. In spite of this long tradition, they have been considered by the majority of crystallographers only as additional parameters for improving the final agreement between calculated and observed structure factors. This point of view is particularly widespread in nonmolecular crystallography, which concerns most mineralogic applications.

As early as the late 1950s the problem of correcting interatomic distances for thermal motion was raised (Cruickshank 1956b, 1956c; Busing and Levy 1957). These corrections, which imply the use of accurate estimates of ADPs, became more important with the improvement of the accuracy of crystal-structure data and

of the possibility of their comparison with reliable theoretical estimates. For instance, for a molecule behaving as a rigid body, a model allowing corrections to be made using only crystal-structure parameters was already proposed by Cruickshank (1956b, 1956c). A more complete version of the rigid-body model was proposed later (Schomaker and Trueblood 1968). Several authors subsequently extended these models to partly rigid molecules (Johnson 1970a, 1970b; Dunitz and White 1973; Trueblood 1978; Schomaker and Trueblood 1984; Dunitz et al. 1988; He and Craven 1993).

Unfortunately, models based on rigid-body behavior of atomic groups can hardly be applied to many inorganic structures and minerals. If only Bragg diffraction data are used, without assuming any special model for vibration (e.g., rigid body, riding or uncorrelated motion, etc.), bond distances cannot be corrected for thermal motion. In these cases, and in agreement with current theory (Busing and Levy 1964; Johnson 1970a, 1970b, 1980; Scheringer 1972), only an estimate of the possible error according to the various models can be obtained. To perform the correction for thermal motion in a general case, it is also necessary to know in addition to the ADPs the correla-

tion tensors between the displacement of the bonded atoms k and l, $U_{kl} = \langle u_k u_l^T \rangle$, which cannot be directly deduced from Bragg diffraction measurements.

Besides correcting bond distances, another important application of ADPs (sometimes rather improperly called thermal parameters) is the well-known rigid-bond test, first proposed by Hirshfeld (1976), which states that along the bond direction, the mean-square displacements of chemically bonded atoms should be essentially the same owing to the difficulty of stretching the bond (see also Willis and Pryor 1975; Downs et al. 1990). On considering the bulk of accurately determined molecular structures, this principle has been shown to hold in most cases, and the only exceptions so far observed indicate coexistence of different bonding schemes (see, for instance, Ammeter et al. 1979; Chandrasekhar and Bürgi 1984; Stebler et al. 1986; Stebler and Bürgi 1987; Dunitz et al. 1988; Hummel et al. 1990) or other kinds of disorder, including twinning and stacking faults. These ideas have been successfully applied to rigid groups in structures of minerals [see, for instance, Downs et al. (1990) and references therein; Kunz and Armbruster (1990); Geiger et al. (1992); Bartelmehs et al. (1995)].

An additional application of displacement parameters in mineralogy concerns their accurate determination in studies of electron density (see, for instance, Spackman et al. 1981; Kihara et al. 1986; Downs and Gibbs 1987; Sawada 1993) or extinction (see, for instance, Downs et al. 1985).

For some crystal structures in which the amplitude of displacement of at least some atoms is large, usually implying the presence of disorder, anharmonic motion, or both, more complex expressions of atomic displacement have been proposed and used (see, for instance, Johnson 1969; Johnson and Levy 1974; Kihara et al. 1986; Sawada 1993). All these expressions include tensors of rank higher than the second.

In view of our interest in the field, which had initially started in molecular crystals [see, for instance, Gramaccioli (1987) and references therein], and following a recent recommendation (Kuhs 1992) for more frequent comparison of theoretical calculations and experimental determinations of generalized ADPs, we extended our harmonic lattice-dynamical calculations of displacement parameters to minerals, initially considering oxides such as corundum, quartz, chrysoberyl, and bromellite, and nesosilicates such as the olivine group and garnets (Pilati et al. 1990c, 1993a, 1993b, 1994, 1995, 1996).

Our results confirm the physical meaning of the accurate crystallographic determination of these parameters and emphasize the possibility of wide application of the rigid-ion lattice-dynamical model to minerals. These conclusions are in agreement with several authors, such as Rao et al. (1988), Dove et al. (1992), Kihara (1993), and Ghose et al. (1994). In view of their actual physical meaning, experimental estimates of ADPs can be considered as a source of precious information on the vibrational behavior of every atom in the crystal in the whole

Brillouin zone. Another interesting result of our calculations concerns the importance of zero-point motion, which in most cases is of the order of one-third to one-half of the total at room temperature.

Using more elaborate schemes such as shell models, several other authors, including Price et al. (1987) and Winkler et al. (1991), have successfully applied lattice dynamics to minerals. A particularly interesting example, because it considers diopside, is provided by Patel et al. (1991), who obtained remarkably good results in the evaluation of thermodynamic functions such as the specific heat and entropy at different temperatures. However, the inadequacy of the rigid-ion model with respect to shell models is generally evident for only the highest frequencies, whereas the lowest vibrational energy levels are reproduced with reasonable accuracy, and these low levels contribute most significantly to thermodynamic functions and displacement parameters. Therefore, if use of lattice dynamics is limited to these applications and appropriate attention (and weight) is given to the lowest frequencies in the optimization process for deriving the empirical potentials, appreciable differences between these models cannot be expected. Recently, rigid-ion models similar to ours were also successfully used by other authors such as Dove et al. (1992) and Catti et al. (1993) in deriving the physical properties of calcite and aragonite.

To extend our calculations to more complex silicates we focused on pyroxenes because of their considerable mineralogic and petrologic interest. Diopside seemed to be particularly useful for our purpose because its structure is relatively simple, good (and pure) natural crystals of this substance are available, and there are several reliable experimental data for comparison. These data include accurate crystal-structure determinations (Clark et al. 1969; Cameron et al. 1973; Finger and Ohashi 1976; Bianchi et al., in preparation), Raman and infrared spectra (Omori 1971; Zulumyan et al. 1976), and thermodynamic functions (Krupka et al. 1985a, 1985b).

PROCEDURE OF CALCULATION

Our calculations follow to the classic rigid-ion lattice-dynamical model, extended to the whole Brillouin zone (for details, see, for instance, Pilati et al. 1990c). Following a well-established scheme, from the second derivatives of the potential energy with respect to the positional coordinates of all the atoms in the primitive unit cell [multiplied by $e^{(2\pi i q r)}$, where q is the wave vector and r is the vector distance between two interacting atoms] the so-called dynamical matrices are built (one for each value of q). The square roots of the eigenvalues of these matrices correspond to the vibrational frequencies of the various normal modes, whereas the components of the eigenvectors characterize the shift and the phase of each particular atom in the normal mode.

From these calculated vibrational frequencies extended to the whole Brillouin zone the phonon density of states can be evaluated; then, by applying statistical thermodynamics with the use of the vibrational partition func-

tion, the values of thermodynamic functions can be easily obtained at different temperatures; from the average energy of each vibrational mode and the eigenvectors of the dynamical matrices, ADPs (as Us) can also be calculated (see, for instance, Willis and Pryor 1975).

We wrote a computer program to assist in these calculations. The routines include several new methods, involving, for example, the evaluation of Coulombic lattice sums and the uneven sampling of the Brillouin zone to obtain a fast convergence (Filippini et al. 1976; Pilati et al. 1990a, 1990b). The program input consists essentially of experimental crystallographic data (unit-cell parameters and atomic fractional coordinates, symmetry space group operations) and information for determining energy, including the atomic charge, type of valence force-field (VFF) empirical potential, and its parameters. It is also possible to refine the empirical potentials so that a best fit to some particular experimental data (such as the vibrational frequencies of a group of minerals) may be obtained.

The calculation of thermodynamic functions deserves some comment. For this calculation, the vibrational partition function and its derivatives can be obtained from the lattice-dynamical evaluation of the phonon density of states. This well-known procedure leads, for instance, to values of specific heat (C_V) and entropy. However, the usual experimental measurements of the specific heat are made at constant pressure (C_P) and not, as the definition of C_V requires, at constant volume. For this reason, the well-known thermodynamic relationship between C_P and C_V is used:

$$C_P - C_V = \alpha^2 T V K_T \qquad (1)$$

where α is the volume-expansion coefficient, V is the volume of the substance, and K_T is the bulk modulus. Because the volume expansion is linked to anharmonicity, the above expression is sometimes regarded as a partial correction for anharmonic behavior.

The problem of evaluating entropy (S) from the partition function and the density of states is more delicate because the statistical mechanical procedure affords $S = \int_0^T C_V / T dT$, whereas the corresponding value $S = \int_0^T C_P / T dT$ at constant pressure is usually referred to, in agreement with the more common measurements of C_P rather than C_V. To evaluate the latter integral as such, even if the value of S at only one temperature is needed, it is necessary to know accurate values of C_P over the whole range from 0 K to that temperature. This requires not only that the calculations must be repeated for a series of temperatures but also accurate values of the volume-expansion coefficient, α, and of the bulk modulus for the whole range of temperatures involved.

However, for evaluating entropy, knowledge of C_P is not strictly necessary. For instance, the following path can be envisaged: State 1 corresponds to the crystal at 0 K and 1 atm (V_0 is the corresponding equilibrium volume under these conditions); state 2 also corresponds to the crystal at 0 K but with volume V_{298} (and the internal

structure) corresponding to that observed at room conditions (1 atm and 298 K); state 3 corresponds to the crystal in equilibrium at room conditions, and state 4 to the crystal in equilibrium at 1 atm and a general value of temperature, T_i (under these conditions, V_{Ti} is the equilibrium volume). Thus, for diopside the above four states are as follows: 1 diopside ($T = 0$ K, $V = V_0$) → 2 diopside ($T = 0$ K, $V = V_{298}$) → 3 diopside ($T = 298$ K, $V = V_{298}$) → 4 diopside (T_i, V_{Ti}).

Because S is a function of state, its value is independent of the path followed. For instance, if we need the value of entropy at room conditions, we should evaluate the variation from state 1 to state 3, knowing that at the starting point $S = 0$, in agreement with the third law, because the structure of diopside is ordered. However, always in agreement with the third law, the variation $S(2) - S(1)$ is zero. If $C_V(298)$ indicates the value of the specific heat, C_V, at temperature T, but with $V = V_{298}$, then $S(3) - S(1) = S(3) - S(2) = \int_0^{298} C_V(298)/T dT$ because V_{298} is constant. The last integral corresponds to the evaluation of entropy at 298 K according to our lattice-dynamical harmonic model from the density of states and the vibrational partition function, on the basis of the volume (in practice, the crystal-structure data) at room temperature. Therefore, within the limits of our model, the value of entropy is immediately obtained for these conditions, with no need to take the $C_P - C_V$ difference into consideration. If the values of entropy at different temperatures are needed, starting from the crystal structure at room temperature, then the step 3 → 4 at constant pressure (1 atm) should also be considered. Therefore,

$$S(4) - S(1) = S(2) - S(1) + S(3) - S(2) + S(4) - S(3)$$

$$= S(2) - S(1) + \int_0^{298} C_V(298)/T dT$$

$$+ \int_{298}^{T_i} C_P/T dT$$

$$S(4) = S(T_i, V_{Ti})$$

$$= \int_0^{298} C_V(298)/T dT + \int_{298}^{T_i} C_V(298)/T dT$$

$$+ \int_{298}^{T_i} C_P/T dT + \int_{298}^{T_i} C_V/T dT$$

$$- \int_{298}^{T_i} C_V/T dT - \int_{298}^{T_i} C_V(298)/T dT$$

$$= \int_0^{T_i} C_V(298)/T dT + \int_{298}^{T_i} (C_P - C_V)/T dT$$

$$+ \int_{298}^{T_i} [C_V - C_V(298)]/T dT. \qquad (2)$$

In Expression 2, the second term, as a first approximation (considering α, V, and K_T as temperature independent), can be written as follows:

$$\int_{298}^{T_i} (C_P - C_V)/T \, dT = \int_{298}^{T_i} \alpha^2 V K_T \, dT$$

$$\approx \alpha^2 V_{298} K_T (T - 298). \qquad (3)$$

TABLE 1. Empirical potentials

		Potential 1	Potential 2
Atomic charge			
Si		−1.566	−1.418
Mg		−1.449	−1.482
Ca		−1.256	−1.337
Stretching potentials			
Si-O	A	2671.197	2798.030
	B	0.75610	0.75624
	C	1.65054	1.64173
Mg-O	A	99.5203	58.0805
	B	1.47964	1.50304
	C	2.17169	2.30494
Ca-O	A	187.389	126.2107
	B	0.98372	1.24017
	C	2.41138	2.40593
O-O (>5.50 Å)	A	6.14300	5.97077
	B	0.87475	0.85146
	C	3.68461	3.67660
Bending potentials			
O-Si-O	A	0.399	0.12569
	B	0.033	−0.62573
	C		1.11716
O-Mg-O	A		0.16446
	B		−0.09038
	C		−0.31814
O-Ca-O	A		−0.05435
Si-O-Si	A	0.121	0.13883
Bending-stretching			
O-Si-O/Si-O	A	−0.190	0.10091
	B	0.012	−0.05480
Stretching-stretching			
Si-O/Si-O		0.276	0.11538

Note: Parameters A, B, and C for Morse functions are given as energy (kJ/mol) = A{exp[−2B(r − C)] − 2exp[−B(r − C)]}, where r is the distance. For angles (β), bending constant K = A + B cos β + C cos² β; if B or C is not given, it is zero. For bending-stretching, K = A + B(β − 109.47°). For coulombic interactions, the reciprocal lattice was sampled up to a limiting value of $d^* = 1.7$ Å⁻¹. The atomic charge of O was calculated by difference to satisfy charge balance. Units of measure are as follows: atomic charge in electrons, parameters A, B, and C for stretching potentials are in units of kilojoules per mole, inverse angstroms, and angstroms, respectively, bending potentials in millidyn-angstroms per squared radian, bending-stretching potentials in millidyns per radian, and stretching-stretching potentials in millidyns per angstrom.

Expression 3 corresponds to an anharmonic correction, which derives from the unit-cell variation between the reference point at room conditions and the new conditions.

The last term in Expression 2 accounts for the variation in specific heat, C_V, with respect to the volume. However, consistent with classical thermodynamics, we obtain

$$(\partial C_V/\partial V_T) = \partial^2 E/\partial T \partial V = [\partial(\partial E/\partial V)_T/\partial T]_V$$

$$= [\partial(T\alpha K_T - P)/\partial T]_V$$

$$= T[\partial(\alpha K_T)/\partial T]_V + \alpha K_T - (\partial P/\partial T)_V \quad (4)$$

where E is the energy of the system. Because, according to thermodynamics, $(\partial P/\partial T)_T = \alpha K_T$, Expression 4 becomes

$$(\partial C_V/\partial V)_T = T[\partial(\alpha K_T)/\partial T]_V. \quad (5)$$

Therefore, if the expansion coefficient and the bulk modulus can be regarded as temperature independent, C_V be-

comes volume independent, and consequently there is no difference between C_V and $C_V(298)$. Accordingly, the last term in Expression 2 vanishes, and we have

$$S(T_i, V_{T_i}) = \int_0^{T_i} C_V(298)/T \, dT + \int_{298}^{T_i} (C_P - C_V)/T \, dT$$

$$\approx \int_0^{T_i} C_V(298)/T \, dT + \alpha^2 V_{298} K_T(T - 298).$$

$$(6)$$

On applying this very simple procedure, the results are quite satisfactory (see below). At extremely high or low temperatures, the disagreement is greater because the values of α, V, and the bulk modulus cannot be considered to be constant, as we have assumed because of the lack of adequate experimental data.

It is well known that α and K_T could be derived from the same potentials and with essentially the same procedure as for V with the use of the quasi-harmonic approximation (see, for instance, Patel et al. 1991). Because the main scope of this paper is restricted to the evaluation of displacement parameters, or of thermodynamic functions starting from crystal data as obtained experimentally under different conditions, and not that of modeling the crystal structure, such calculations (which are very lengthy) have been omitted.

ANALYSIS OF RESULTS AND DISCUSSION

With the assumption that the charge is the same for all the atoms of the same element (in the absence of a more detailed criterion), with the exception of O (the charge of which is derived from the overall balance for each structure), all parameters of the two force fields used here for diopside (including the atomic charge) and reported in Table 1 were obtained on the basis of a best fit to the vibrational frequencies of quartz and nesosilicates such as the most common members of the olivine group (forsterite, fayalite, monticellite, tephroite); the second force field was derived from a fit to the vibrational frequencies of a considerably wider set of substances, including (besides quartz and the olivine group) some garnets, andalusite, and also some oxides containing Al or Be, such as corundum, chrysoberyl, and bromellite. Most of these data are Raman- and infrared-active frequencies obtained by different authors (for additional details and reference to the sources, see Pilati et al. 1990c, 1993a, 1993b, 1994, 1995, 1996). Also the lowest branches of the phonon dispersion curves were included when available, as they were for quartz, forsterite, and andalusite. It is interesting to note that no specific experimental data for diopside were included in our best-fit procedure. Therefore, our success in reproducing several physical properties of this substance emphasizes the transferability of these potentials from other substances. As it is clear from Table 1, the potentials include Morse-type functions for stretching or O-O interaction, plus three-body interactions described as bond bending, bending-stretching, or stretching-stretching.

The calculated Raman- and infrared-active frequencies are reported in Table 2, together with the corresponding experimental results obtained by Zulumyan et al. (1976) and Omori (1971). The agreement is remarkable, especially for the low-frequency range, and is in line with the expected performance of a rigid-ion model and with the weighting scheme used to derive the potential parameters, which underlines the importance of low frequencies. (See above: In the optimization procedure, a weight inversely proportional to the square of the frequency was assigned to each observation.) Therefore, the success of these lattice-dynamical calculations and the transferability of empirical potentials within wide groups of different substances are confirmed. The good transferability of empirical potentials agrees with the results published by other authors, such as Winkler et al. (1991) and Patel et al. (1991).

On considering spectral data in some detail, most of the Raman-active A_g modes up to about 550 cm^{-1} reported by Zulumyan et al. (1976) agree very well with our calculations; however, of the two frequencies observed at 235 and 256 cm^{-1} (both quite weak), one should probably be dropped from the list of fundamentals. On the other hand, a fundamental frequency at about 305 cm^{-1}, which is missing in the experimental data, should be expected according to our model. Above 600 cm^{-1}, as for the other symmetry labels, the agreement becomes decidedly worse, as expected for a rigid-ion model (see above).

For the Raman-active B_g modes, the agreement with the experimental data below 600–700 cm^{-1} is also very good, especially for the results of the first set of potentials. Here, there is some doubt about the existence of the fundamental frequencies of medium intensity at 198 and 517 cm^{-1} reported by Zulumyan et al. (1976); on the contrary, a frequency near 150 and another one near 415 cm^{-1}, which are missing in the experimental data, are expected to occur.

The agreement of the infrared-active A_u frequencies is not as good as that for the other symmetry denominations, and consequently there are fewer reasons for doubting Zulumyan's selection of fundamentals, although the frequency at 305 cm^{-1}, of very weak intensity, does not seem to match our model. The lowest B_u frequencies, which are also infrared-active, have not yet been measured on a single crystal, but the powder absorption spectrum shows peaks at 140, 150–175, and 245 cm^{-1} the attribution of which to B_u modes seems to be the only possibility, in good agreement with our calculations. However, the very low-frequency (and weak) peak observed in the powder spectrum at 75 cm^{-1} cannot be reconciled with our model and might be spurious. Such a conclusion finds support on considering that, owing to the overwhelming importance of the lowest frequencies, the presence of an optic branch so low would make the estimates of both thermodynamic functions and ADPs markedly higher than our present estimates (this does not affect the experimental values).

ADPs at room temperature (298 K), calculated for all the independent atoms in the crystal structure with the

TABLE 2. Vibrational spectra (cm^{-1}) at room temperature

Obs(1)	Obs(2)	Calc(1)	Calc(2)
		A_g	
140		129	129
182		193	189
235		211	207
256		246	244
		306	302
326		327	332
360		356	359
390		394	394
508		526	514
530		557	559
668			
		770	716
858		906	941
1016		969	965
1050		998	991
		A_u(TO)	
220	220	205	195
240	245	232	232
305	292	279	291
335	335	351	352
363	366	366	365
410	395	412	411
465	470–482	521	493
505		549	557
		564	574
670	670	703	664
915	920	864	907
960	966	968	963
1070	1095	1015	1015
		B_g	
118		119	104
169		148	141
198		175	159
232		229	225
305		300	295
328		316	320
358		352	349
395		375	381
468		413	415
517		454	462
560		548	560
		601	609
710		738	689
920		862	907
1015		960	953
1048		1027	1018
		B_u(TO)	
	(75?)		
	140	139	122
	150–175	185	175
	245	262	254
282	292	274	274
295	310	310	316
325	335	328	329
385	366	369	366
430	427	424	426
455		467	446
515	510–512	511	508
630	630	715	664
860	920	894	935
975	985	961	965
1060	1074	987	978
		R (%)	
		5.0	4.5

Note: The calculated values correspond to the force fields reported in Table 1. The value of R (= Σ|freq$_{obs}$ − freq$_{calc}$|/Σ freq$_{obs}$) is reported below each column. Obs(1) = single-crystal data from Zulumyan et al. (1976); obs(2) = powder absorption data, including Omori's (1971), partly elaborated by Zulumyan et al. (1976). For these powder data, the symmetry labeling is uncertain, and in this table it is assigned tentatively on the basis of the best agreement with the single-crystal observations or with our calculations.

TABLE 3. Anisotropic displacement parameters ($\times 10^4$) for diopside at 298 K

Atom		U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	B_{eq} (Å²)
Ca	obs (1)	89	0	−3	56	0	53	0.58
	calc (1)	89	0	−10	61	0	63	0.61
	obs (2)	93	0	−1	60	0	59	0.59
	obs (3)	90	0	−2	57	0	58	0.58
	obs (4)	96	0	0	59	0	58	0.59
	calc (2)	109	0	−13	65	0	66	0.69
	z.p. (1)	27	0	1	22	0	22	0.19
Mg	obs (1)	59	0	11	57	0	46	0.43
	calc (1)	52	0	9	55	0	48	0.41
	obs (2)	64	0	12	65	0	56	0.49
	obs (3)	54	0	9	55	0	46	0.42
	obs (4)	61	0	11	54		45	0.42
	calc (2)	59	0	12	58	0	48	0.44
	z.p. (1)	25	0	6	24	0	22	0.19
Si	obs (1)	39	3	9	46	2	37	0.32
	calc (1)	35	2	7	43	1	39	0.31
	obs (2)	43	3	1	50	2	45	0.37
	obs (3)	37	3	8	44	2	37	0.32
	obs (4)	43	2	11	48	2	40	0.34
	calc (2)	37	3	8	46	1	40	0.33
	z.p. (1)	15	1	4	16	0	16	0.13
O1	obs (1)	42	0	8	74	−3	58	0.47
	calc (1)	41	1	8	70	−2	58	0.46
	obs (2)	52	1	9	82	−3	71	0.55
	obs (3)	52	1	10	82	−3	68	0.54
	obs (4)	47	1	12	71	0	64	0.48
	calc (2)	43	1	8	76	−4	60	0.48
	z.p. (1)	21	1	5	33	0	30	0.23
O2	obs (1)	86	22	15	61	6	74	0.59
	calc (1)	79	21	14	60	7	78	0.58
	obs (2)	100	25	17	65	7	89	0.68
	obs (3)	99	24	17	66	6	85	0.67
	obs (4)	94	23	18	67	6	70	0.62
	calc (2)	89	23	15	60	6	78	0.61
	z.p. (1)	36	8	8	27	3	37	0.26
O3	obs (1)	59	1	15	82	21	58	0.53
	calc (1)	48	−2	10	71	15	53	0.46
	obs (2)	73	1	21	93	24	66	0.61
	obs (3)	72	1	20	92	23	65	0.60
	obs (4)	65	1	18	90	18	53	0.54
	calc (2)	49	−2	10	73	15	50	0.46
	z.p. (1)	26	0	7	31	7	24	0.21

Note: The temperature factor is in the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$. Obs(1) is data from Bianchi et al. (personal communication), conventional refinement using usual spherical form factors; obs(2) is same data and authors as for obs(1), from crystal-structure refinement: here, a rigid pseudoatom model was used, including terms up to octupole (Stewart 1976); obs(3) is same data, authors, and procedure as for obs(2), also refining the radial density function parameter a for each pseudoatom (see Stewart 1976); obs(4) is our own data, conventional refinement using spherical form factors. The natural crystal used (from Ala Valley) contains about 0.06 at% Fe substituting for Mg. Calc(1) and calc(2) data were calculated using the force fields with the corresponding number in Table 1; z.p.(1) is zero-point contribution evaluated according to the force field 1 (the contribution obtained from the force field 2 is nearly identical). For all experimental data shown in this table, the reported standard deviations are of the order of unity on the last digit, or even considerably lower; however, further digits are not reported here because their accuracy may be questionable.

use of both empirical potentials reported in Table 1, are reported in Table 3. For comparison, the same table reports the corresponding experimental data obtained from some particularly high-quality crystal-structure refinements. Details of the crystal-structure analysis are reported in Tables 4–8.[1]

On the whole, all the observed ADP values reported in Table 3 are in reasonable agreement with our calcula-

tions; this agreement is especially evident for the results of our potential 1, which is superior in interpreting the behavior of the Ca atom. For the bridging O atom O3, the agreement is somewhat worse than for the other atoms; however, even here an essential agreement (within about 15% on the average) is reached. Most of the uncertainty of the calculated values depends on the convergence of the Brillouin-zone sampling (see Filippini et al. 1976; Pilati et al. 1990b); the accuracy for ADPs is about 3%, and for thermodynamic functions it is <0.1%. These results prove the essential correctness and physical significance of both our lattice-vibrational model and the experimental ADPs, the latter of which were obtained from accurate crystal-structure refinement: The agreement between the theoretical and experimental data corresponds to similar results we obtained for organic molecular crystals and for several other minerals (Gramaccioli 1987; Pilati et al. 1990c, 1993a, 1993b, 1994, 1995, 1996).

From comparison of the estimated values of the ADPs reported in Table 3, nonnegligible differences among the several sets of experimental data are easily noticed. These differences, which sometimes exceed the standard deviation by a factor of six, occur even between sets that derive from different kinds of refinement of the same diffracted X-ray data. Because our obs(4) set does not appreciably differ from obs(1), no particular discussion concerning our set is needed.

To determine which is the best set of experimental ADPs to be compared with the results of our calculations, the agreement per se is not a reliable criterion; therefore, some independent measure should be found. Here, for instance, it might be interesting to apply Hirshfeld's rigid-bond criterion, the results of which, applied to the Si-O bonds (which should be rigid), are shown in Table 9. For the sets obs(1) and obs(2) (considered together) and our calculations, the absolute values of the mean-square differences along the Si-O bonds range from 25 to 87 × 10^{-5} Å², and from 51 to 70 × 10^{-5} Å², respectively, i.e., they are even below the accepted limit of 125 × 10^{-5} Å² found by Downs et al. (1990) for framework structures. Instead, for the obs(3) set they are about twice as large (from 131 to 156 × 10^{-5} Å²), and because it is difficult to imagine why such large differences should exist, there are good reasons for not accepting the corresponding estimates of the ADPs; in addition, our calculations give an idea of what such differences should be in this case, confirming Hirshfeld's test and its limits on lattice-dynamical grounds. It should be noted that Bianchi et al. (personal communication) independently found the refinement corresponding to obs(3) to be not entirely satisfactory owing to strong correlation between some of the refined parameters.

TABLE 9. Rigid-bond test (Hirshfeld 1976) and corrected values for thermal motion of Si-O distances in diopside at room temperature

Bond	Length (Å)		Force constant (mdyne/Å)	$\Delta(rms) \times 10^5$ (Å²)			
	Uncorr.	Corr.		Calc	Obs (1)	Obs (2)	Obs (3)
Si-O1	1.600	1.604	5.836	70	33	88	156
Si-O2	1.586	1.591	6.019	70	63	77	136
Si-O3	1.670	1.673	4.987	57	80	25	135
Si-O3'	1.687	1.690	4.789	51	50	87	131

Note: All observed data from Bianchi et al. (personal communication). Calculated values (298 K) according to our force field 1.

In Table 3, the zero-point (z.p.) contribution, evaluated according to our calculations, is also reported for each component of the U tensors. As for all the silicates and oxides that we examined, this contribution (35% of the room-temperature value) is remarkably large and far from being negligible. Unfortunately, too few reliable measurements of minerals at very low temperature are available to verify our theoretical predictions; in any case, our estimates for minerals confirm the experimental results obtained by Smith et al. (1986) and, more recently, by Pavese et al. (1995). For organic crystals such measurements are much more common, and for benzene (Filippini and Gramaccioli 1989) at 15 and 4.2 K our calculations closely matched the experimental data obtained by Jeffrey et al. (1987) and David and Ibberson (1989). Because the Debye temperature for minerals is considerably higher than for most organic crystals, which have quite large zero-point contributions (for instance, the zero-point motion contribution to the ADPs of the C atoms of benzene at 123 K is 31%), there was reason to expect a result of the same order of magnitude for minerals at room temperature. In Table 10, the experimental values of the equivalent Bs at various temperatures are reported and compared with our calculations. The agreement is good.

Another interesting observation can be drawn concerning the possibility of correcting the bond distances for thermal motion. According to Johnson (1970a, 1970b, 1980) and Scheringer (1972) we have $r_c = r_o + [trace (Z) - r_o^T Z r_o / r^2]/2 r_o$, where r_c and r_o are the corrected and the uncorrected distances, respectively, between the atoms i and k, r_o is the vector corresponding to the atomic distance, and Z is a matrix defined as $Z = U_i + U_k - U_{ik} - U_{ki}$, in which, besides the ADP tensors $U_i = \langle u_i u^T_i \rangle$ and $U_k = \langle u_k u^T_k \rangle$, we also have the correlation tensors $U_{ik} = \langle u_i u^T_k \rangle$. The correlation tensors, we have seen, cannot be obtained directly from Bragg diffraction measurements. However, these tensors can be evaluated from lattice dynamics together with the usual Us (see, for instance, Willis and Pryor 1975, Eq. 4.86b, in which polarization vectors for different atoms should replace those for the same atom), and if our calculations acceptably agree with the experimental Us, on the basis of the close similarity in the calculating procedure and routines, there is good reason to believe that the estimates of the correlation tensors are also correct.

Applying these considerations and procedures to the bond distances in diopside gives the results at room temperature (298 K) reported in the third column of Table 9. As with other silicates we have examined (Pilati et al. 1990c, 1995), and with quartz (Pilati et al. 1994), the correction amounts to a few thousandths of an angstrom (0.003–0.007 Å). Table 11 shows the corrected distances for diopside at various temperatures, starting from the crystal-structure data at these temperatures reported by Cameron et al. (1973); at 1273 K the correction is of the order of 0.01–0.02 Å. Here, a curious phenomenon can be observed, especially for the Si-O bonds: The uncorrected values are almost constant, whereas the corrected values increase with increasing temperature. This phenomenon is due to an essential rocking motion of the nearly rigid SiO₄ tetrahedron, which tends to lower the values of the uncorrected distances, as it does for rigid molecules. This apparent shrinkage nearly equals the increase in the real values of the Si-O bond lengths with increasing temperature. Our observations are in agreement with the results of Downs et al. (1992), who observed an apparent average shrinkage of 0.005 Å for the Si-O bonds of several silicates at room temperature; these values either are invariant or show a light contraction with increasing temperature. At higher temperature (1250 K), according to those authors, the rigid-body correction to the Si-O bonds amounts to as much as 0.03 Å.

Calculated values of thermodynamic functions such as the specific heat, C_P, and entropy, S, at different temperatures according to our model and procedure are reported in Tables 12 and 13, where they are compared with the corresponding experimental values obtained by Krupka

TABLE 10. Equivalent isotropic B values (Å²) for diopside at different temperatures

T(K)	297 CSP	673 CSP	673 Calc	973 FO	973 CSP	973 Calc	1123 CSP	1123 Calc	1273 CSP	1273 Calc
Ca	0.514(7)	0.141(2)	0.126	0.226(4)	0.214(2)	0.191	0.237(2)	0.225	0.283(2)	0.258
Mg	0.26(1)	0.96(2)	0.84	0.150(4)	0.140(2)	0.133	0.157(2)	0.160	0.189(2)	0.187
Si	0.228(7)	0.80(1)	0.62	0.115(3)	0.112(2)	0.099	0.118(1)	0.119	0.137(1)	0.140
O1	0.33(2)	0.105(3)	0.90	0.153(6)	0.152(3)	0.141	0.165(2)	0.167	0.195(3)	0.195
O2	0.46(2)	0.139(3)	0.118	0.202(7)	0.196(4)	0.179	0.223(3)	0.213	0.262(4)	0.244
O3	0.39(2)	0.122(3)	0.90	0.165(6)	0.171(3)	0.139	0.186(3)	0.166	0.214(4)	0.191

Note: CSP = observed data from Cameron et al. 1973. FO = observed data from Finger and Ohashi 1976. Calc = our lattice-dynamical calculations, from potential 1, using the experimental unit-cell parameters and atomic coordinates found at different temperatures by Cameron et al. 1973.

TABLE 11. Bond distances (Å) at higher temperatures, uncorrected and corrected for thermal motion

	T = 673 K		T = 973 K	
	Uncorr.	Corr.	Uncorr.	Corr.
Ca-O1	2.378	2.386	2.391	2.403
Ca-O2	2.357	2.368	2.366	2.381
Ca-O3	2.571	2.579	2.578	2.589
Mg-O1	2.136	2.142	2.146	2.156
Mg-O1'	2.067	2.075	2.070	2.081
Mg-O2	2.063	2.072	2.077	2.090
Si-O1	1.601	1.608	1.599	1.609
Si-O2	1.586	1.595	1.586	1.599
Si-O3	1.671	1.677	1.670	1.678
Si-O3'	1.687	1.693	1.688	1.696
	T = 1123 K		T = 1273 K	
	Uncorr.	Corr.	Uncorr.	Corr.
Ca-O1	2.394	2.407	2.399	2.414
Ca-O2	2.368	2.385	2.370	2.390
Ca-O3	2.580	2.593	2.587	2.601
Mg-O1	2.151	2.162	2.160	2.172
Mg-O1'	2.069	2.082	2.075	2.090
Mg-O2	2.081	2.096	2.086	2.103
Si-O1	1.603	1.615	1.601	1.614
Si-O2	1.583	1.598	1.586	1.603
Si-O3	1.670	1.679	1.671	1.682
Si-O3'	1.690	1.699	1.690	1.700

Note: Calculations of Us and of the correlation tensors were performed using potential 1. Standard deviations are about 0.002 Å for Si-O and Mg-O bonds, and 0.002–0.003 Å for Ca-O bonds.

TABLE 12. Specific heat at various temperatures [J/(mol·K)]

T(K)	C_P obs	C_v calc (1)	C_v calc (1)	C_v calc (2)	C_P calc*
5	0.009	0.01	0.01	0.01	
10	0.082	0.08	0.08	0.09	
20	0.755	0.85	0.85	1.07	
30	2.790	3.36	3.34	3.99	
40	6.799	7.84	7.79	8.77	
50	12.42	13.88	13.79	14.93	
60	19.29	21.06	20.90	22.05	
80	35.28	37.61	37.25	38.22	
100	52.40	54.70	53.98	54.72	55.00
120	69.21	70.96	70.10	70.68	
140	84.82	86.01	85.00	85.52	
160	99.09	99.71	98.56	99.07	
180	112.1	112.1	110.84	111.36	
200	123.7	123.4	121.96	122.49	
240	143.8	142.9	141.22	141.75	
280	160.4	159.2	157.15	157.65	
298	166.8	165.5	163.39	163.87	166.69**
320	174.0	172.6	170.35	170.80	
360	185.5	183.9	181.30	181.69	
400	195.5	193.3	190.39	190.73	
500	214.4	210.6	207.05	207.30	209.93
600	224.3	222.2	217.90	218.07	
700	234.0	230.2	225.21	225.34	228.38
800	239.4	236.1	230.31	230.42	
900	241.8	240.4	233.99	234.08	
1000	247.0	243.9	236.72	236.79	240.71
1100	249.0	246.7	238.79	238.85	
1200	251.0	249.0	240.40	240.45	
1300	252.8	251.0	241.67	241.71	

Note: Observed values of C_p from Krupka et al. (1985a, 1985b). The calculated values C_v calc (1) and C_v calc (2) correspond to the specific heat at constant volume calculated according to potential 1 or 2, respectively. The values of C_p calculated by us (C_p calc) were obtained by adding the $C_p - C_v$ difference, $\alpha^2 K_T VT$, to the corresponding calculated value of C_v (here evaluated using potential 1). For this purpose, the average value of the volume expansion coefficient $\alpha = 31 \times 10^{-6}$ K^{-1} measured by Finger and Ohashi (1976) from 24 to 1000 °C was assumed to be constant from 100 to 1300 K; below 100 K, a linear interpolation down to a zero value at 0 K was assumed. For the bulk modulus the value $K_T = 1.13$ Mbar found by Levien et al. (1979) was used.
* These calculated values of C_p are from Patel et al. 1991.
** Actual temperature was 300 K.

et al. (1985a, 1985b) and with the calculated values of Patel et al. (1991), who used a shell model. The agreement is remarkably good: For instance, at room temperature (298 K) S and C_P disagree with the corresponding experimental data by only 0.4 and 0.8%, respectively, and the situation remains just as satisfactory up to 1000 K and above. This is more proof of the reliability of lattice-dynamical calculations and of our procedure in particular. The excellent results found by other authors such as Winkler et al. (1991), Patel et al. (1991) using lattice dynamics are also confirmed, even those concerning transferability of potentials at least within a group that includes several oxides and silicates. In particular, as we have already emphasized, the potentials used here have not involved any particular fit to the properties of diopside, neither involving the observed frequencies nor the Debye temperature. This fit is instead essential in many applications of vibrational partition functions to crystals, such as Kieffer's (1979a, 1979b, 1979c, 1980).

Unfortunately, for minerals there are only a few determinations of the acoustic branches of the phonon dispersion curves, which are the most important for comparing the results of lattice-dynamical calculations or for fitting the potentials, and the great majority of experimental data useful for these purposes consist of Raman and infrared spectroscopic measurements. A general inconvenience is that single-crystal data are relatively scarce, whereas most scientific work is based on powder data, where all modes of different symmetry are collected together, not permit-

ting a reliable assignment. Moreover, there are still insufficient (and often inaccurate) measurements, particularly concerning the lowest frequencies. For silicates, especially, the lowest optic frequencies are of the order of 150 cm^{-1}, and precise measurements in this region of the spectrum with conventional instruments are difficult. In some cases there are also frequencies of the order of 100 cm^{-1}, or still lower, that are even more difficult to find and measure exactly. After having examined several cases, our present opinion is that if several precise measurements of low frequencies and phonon dispersion curves (especially at low temperature) were available for a large group of minerals, it would be possible to derive sets of reliable empirical potentials, which would result in agreement with experimental data beyond any present expectation.

With respect to other statistical-mechanical procedures, such as the one proposed by Kieffer (1979a, 1979b, 1979c, 1980) that has been extensively applied to minerals, the Born–von Kármán lattice-dynamical model is

TABLE 13. Entropy at various temperatures [J/(mol·K)]

T(K)	S_{obs}	S_{calc} (1)	S_{calc} (2)	S_{calc} (1)*	S_{calc}**
5	0.003	0.00	0.00	0.00	
10	0.019	0.03	0.03	0.03	
20	0.234	0.25	0.30	0.25	
30	0.866	0.99	1.22	0.99	
40	2.176	2.52	2.98	2.52	
50	4.269	4.88	5.58	4.88	5.00†
60	7.124	8.01	8.62	8.01	
80	14.81	16.73	17.74	16.73	
100	24.52	25.42	26.67	26.84	
120	35.57	36.86	38.26	38.13	
140	47.43	48.94	50.45	50.07	
160	59.70	61.33	62.92	62.32	
180	72.14	73.80	75.47	74.65	
200	84.56	86.22	88.15	86.92	
240	108.9	110.93	112.79	111.35	
280	132.4	134.23	136.18	134.36	
298	142.7	143.26	145.19	143.26	147.00‡
320	154.7	156.40	158.42	153.24	
360	175.9	177.40	179.47	176.96	
400	196.3	197.30	199.40	196.54	
500	242.5	242.41	244.61	240.96	243.94
600	282.3	281.91	284.15	279.74	
700	317.4	317.12	319.40	314.23	317.89
800	348.7	348.26	350.56	344.66	
900	377.0	376.33	378.65	372.01	
1000	402.7	401.85	404.18	396.81	401.74
1100	426.5	425.24	427.57	419.48	
1200	448.5	446.81	449.15	440.33	
1300	469.1	466.82	469.16	459.63	

Note: Observed values of S from Krupka et al. (1985a, 1985b). The calculated values S_{calc} (1) and S_{calc} (2) correspond to the entropy calculated according to potential 1 or 2, respectively. The values of entropy calculated by us and reported in columns 3 and 4 were corrected for anharmonicity (thermal expansion) for temperatures above 80 K, assuming the values reported above (as temperature independent) for the volume-expansion coefficient and the bulk modulus. The calculated values in column 5 were not corrected for this effect.
 * Values uncorrected for thermal expansion (see above).
 ** These calculated values of S_{calc} are from Patel et al. 1991.
 † The value reported by Patel et al. (1991) for T = 100 K probably refers instead to T = 50 K.
 ‡ Actual temperature was 300 K.

not only more accurate but requires no fit to several specific experimental data for a single phase: For instance, if transferability of potentials is further confirmed, and better sets are obtained, it could be possible to derive thermodynamic properties of a mineral from only the crystal structure. In the future such a derivation might be possible even without such data, if procedures for the modeling of crystal structures are adequately extended to allow prediction of all the possible phases of a certain substance and their fields of stability.

As a final remark, because the displacements at 0 K are far from negligible owing to their physical insignificance, the models with motionless atoms at 0 K should be abandoned.

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REFERENCES CITED

Ammeter, J.H., Bürgi, H.B., Gamp, E., Meyer-Sandrin, V., and Jensen, W.P. (1979) Static and dynamic Jahn-Teller distortions in CuN_6 complexes: Crystal structure and EPR spectra of complexes between copper(II) and rigid tridentate cis,cis-1,3,5-triaminocyclohexane. Inorganic Chemistry, 18, 733–750.

Bader, R.F.W. (1990) Atoms in molecules: A quantum theory. International Series of Monographs on Chemistry, 22, 438 p. Oxford University Press, Oxford, U.K.

Bartelmehs, K.L., Downs, R.T., Gibbs, G.V., Boisen, M.B., Jr., and Birch, J.B. (1995). Tetrahedral rigid-body motion in silicates. American Mineralogist, 80, 680–690.

Busing, W.R., and Levy, H.A. (1957) Neutron diffraction study of calcium hydroxide. Journal of Chemical Physics, 26, 563–568.

———(1964) The effect of thermal motion on the estimates of bond lengths from diffraction measurements. Acta Crystallographica, 17, 142–146.

Cameron, M., Sueno, S., Prewitt, C.T., and Papike, J.J. (1973) High-temperature crystal chemistry of acmite, diopside, hedenbergite, jadeite, spodumene, and ureyite. American Mineralogist, 58, 594–618.

Catti, M., Pavese, A., and Price, G.D. (1993) Thermodynamic properties of $CaCO_3$ calcite and aragonite: A quasi-harmonic calculation. Physics and Chemistry of Minerals, 19, 472–479.

Chandrasekhar, K., and Bürgi, H.B. (1984) Dynamic processes in crystals examined through difference vibrational parameters ΔU: The low-spin-high-spin transition in tris(dithiocarbamato)iron(III) complexes. Acta Crystallographica, B40, 387–397.

Clark, J.R., Appleman, D.E., and Papike, J.J. (1969) Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements. Mineralogical Society of America Special Paper, 2, 31–50.

Cruickshank, D.W.J. (1956a) The determination of the anisotropic thermal motion of atoms in crystals. Acta Crystallographica, 9, 747–753.

———(1956b) The analysis of anisotropic thermal motion of molecules in crystals. Acta Crystallographica, 9, 754–756.

———(1956c) Errors in bond lengths due to rotational oscillation of molecules. Acta Crystallographica, 9, 757–758.

David, W.I.F., and Ibberson, R.M. (1989) ISIS facility Annual Report, 43–46. Swindon Press, Swindon, U.K.

Dove, M.T., Winkler, B., Leslie, M., Harris, M.J., and Salje, E.K.H. (1992) A new interatomic potential model for calcite: Applications to lattice dynamics studies, phase transition, and isotope fractionation. American Mineralogist, 77, 244–250.

Downs, J.W., Ross, F.K., and Gibbs, G.V. (1985) The effect of extinction on the refined structural parameters of crystalline BeO in a neutron and X-ray diffraction study. Acta Crystallographica, B41, 425–431.

Downs, J.W., and Gibbs, G.V. (1987) An exploratory examination of the electron density and electrostatic potential of phenakite. American Mineralogist, 72, 769–777.

Downs, R.T., Gibbs, G.V., and Boisen, M.B., Jr. (1990) A study of the mean-square displacement amplitudes of Si, Al, and O atoms in framework structures: Evidence for rigid bonds, order, twinning, and stacking faults. Americans Mineralogist, 75, 1253–1267.

Downs, R.T., Gibbs, G.V., Bartelmehs, K.L., and Boisen, M.B., Jr. (1992) Variations of bond lengths and volumes of silicate tetrahedra with temperature. American Mineralogist, 77, 751–757.

Dunitz, J.D., and White, D.N.J. (1973) Non-rigid-body thermal motion analysis. Acta Crystallographica, A29, 93–94.

Dunitz, J.D., Schomaker, V., and Trueblood, K.N. (1988) Interpretation of atomic displacement parameters from diffraction studies of crystals. Journal of Physical Chemistry, 92, 856–867.

Filippini, G., Gramaccioli, C.M., Simonetta, M., and Suffritti, G.B. (1976) Lattice-dynamical application to crystallographic problems: Consideration of the Brillouin-zone sampling. Acta Crystallographica, A32, 259–264.

Filippini, G., and Gramaccioli, C.M. (1989) Benzene crystals at low temperature: A harmonic lattice-dynamical calculation. Acta Crystallographica, A45, 261–263.

Finger, L.W., and Ohashi, Y. (1976) The thermal expansion of diopside to 800 °C and a refinement of the crystal structure at 700 °C. American Mineralogist, 61, 303–310.

Geiger, C.A., Armbruster, Th., Lager, G.A., Jiang, K., Lottermoser, W., and Amthauer, G. (1992) A combined temperature dependent ^{57}Fe Mössbauer study of synthetic almandine: Evidence for the Goldanskii-Karyagin effect. Physics and Chemistry of Minerals, 19, 121–126.

Ghose, S., Choudhury, N., Chaplot, S.L., Pal Chowdury, C., and Sharma, S.K. (1994) Lattice dynamics and Raman spectroscopy of protoenstatite $Mg_2Si_2O_6$. Physical Chemistry of Minerals, 20, 469–477.

Gramaccioli, C.M. (1987) Spectroscopy of molecular crystals and crystallographic implications. International Reviews in Physical Chemistry, 6(4), 337–349.

He, X.M., and Craven, B. (1993) Internal vibrations of a molecule consisting of rigid segments: I. Non-interacting internal vibrations. Acta Crystallographica, A49, 10–22.

Hirshfeld, F.L. (1976) Can X-ray data distinguish bonding effects from vibrational smearing? Acta Crystallographica, A32, 239–244.

Hummel, W., Raselli, A., and Bürgi, H.B. (1990) Analysis of atomic displacement parameters and molecular motion in crystals. Acta Crystallographica, B46, 683–692.

Jeffrey, G.A., Ruble, J.R., McMullan, R.K., and Popie, J.A. (1987) The crystal structure of deuterated benzene. Proceedings of the Royal Society, A125, 401–419.

Johnson, C.K. (1969) Addition of higher cumulants to the crystallographic structure-factor equation: A generalized treatment for thermal-motion effect. Acta Crystallographica, A25, 187–194.

——— (1970a) Generalized treatments for thermal motion. In B.T.M. Willis, Ed., Thermal neutron diffraction, p. 132–160. Oxford University Press, Oxford, U.K.

——— (1970b) An introduction to thermal motion analysis. In F.R. Ahmed, Ed., Crystallographic computing, p. 220–226. Munksgaard, Copenhagen, Denmark.

——— (1980) Thermal motion analysis. In R. Diamond, S. Ramaseshan, and K. Venkatesan, Eds., Computing in crystallography, p. 14.01–14.19. Indian Academy of Sciences, Bangalore, India.

Johnson, C.K., and Levy, H.A., Eds. (1974) International tables for X-ray crystallography, vol. IV, p. 311–336. Kynoch, Birmingham, U.K.

Kieffer, S.W. (1979a) Thermodynamics and lattice vibrations of minerals: 1. Mineral heat capacities and their relationships to simple lattice vibrational models. Review of Geophysics and Space Physics, 17, 1–19.

——— (1979b) Thermodynamics and lattice vibrations of minerals: 2. Vibrational characteristics of silicates. Review of Geophysics and Space Physics, 17, 20–34.

——— (1979c) Thermodynamics and lattice vibrations of minerals: 3. Lattice dynamics and an approximation for minerals with application to simple substances and framework silicates. Review of Geophysics and Space Physics, 17, 35–38.

——— (1980) Thermodynamics and lattice vibrations of minerals: 4. Application to chain and sheet silicates and orthosilicates. Review of Geophysics and Space Physics, 18, 862–886.

Kihara, K. (1993) Lattice dynamical calculations of anisotropic temperature factors of atoms in quartz, and the structure of β-quartz. Physics and Chemistry of Minerals, 19, 492–501.

Kihara, K., Matsumoto, T., and Imamura, M. (1986) High-order thermal-motion tensor analysis of tridymite. Zeitschrift für Kristallographie, 177, 39–52.

Krupka, K.M., Robie, R.A., Hemingway, B.S., Kerrick, D.M., and Ito, J. (1985a) Low-temperature heat capacities and derived thermodynamic properties of anthophyllite, diopside, enstatite, bronzite, and wollastonite. American Mineralogist, 70, 249–260.

Krupka, K.M., Hemingway, B.S., Robie, R.A., and Kerrick, D.M. (1985b) High-temperature heat capacities and derived thermodynamic properties of anthophyllite, diopside, dolomite, enstatite, bronzite, talc, tremolite, and wollastonite. American Mineralogist, 70, 261–271.

Kuhs, W.F. (1992) Generalized atomic displacements in crystallographic structure analysis. Acta Crystallographica, A48, 80–98.

Kunz, M., and Armbruster, T. (1990) Difference displacement parameters in alkali feldspars: Effect of (Si,Al) order-disorder. American Mineralogist 75, 141–149.

Levien, L., Weidner, D.J., and Prewitt, C.T. (1979) Elasticity of diopside. Physics and Chemistry of Minerals, 4, 105–113.

Omori, K. (1971) Analysis of the infrared absorption spectrum of diopside. American Mineralogist, 56, 1607–1616.

Patel, A., Price, G.D.,and Mendelssohn, M.J. (1991) A computer simulation approach to modelling the structure, thermodynamics and oxygen isotope equilibria of silicates. Physical Chemistry of Minerals, 17, 690–699.

Pavese, A., Artioli, G., and Prencipe, M. (1995) X-ray single-crystal diffraction study of pyrope in the temperature range 30–973 K. American Mineralogist, 80, 457–464.

Pilati, T., Bianchi, R., and Gramaccioli, C.M. (1990a) Evaluation of Coulombic lattice sums for vibrational calculations in crystals: An extension of Bertaut's method. Acta Crystallographica, A46, 309–315.

——— (1990b) Evaluation of atomic displacement parameters by lattice-dynamical calculations: Efficiency in Brillouin-zone sampling. Acta Crystallographica, A46, 485–489.

——— (1990c) Lattice-dynamical estimation of atomic thermal parameters for silicates: Forsterite α-Mg_2SiO_4. Acta Crystallographica, B46, 301–311.

Pilati, T., Demartin, F., Cariati, F., Bruni, S., and Gramaccioli, C.M. (1993a) Atomic thermal parameters and thermodynamic functions for chrysoberyl ($BeAl_2O_4$) from vibrational spectra and transfer of empirical force fields. Acta Crystallographica, B49, 216–222.

Pilati, T., Demartin, F., and Gramaccioli, C.M. (1993b) Atomic thermal parameters and thermodynamic functions for corundum (α-Al_2O_3) and bromellite (BeO): A lattice-dynamical estimate. Acta Crystallographica, A49, 473–480.

——— (1994) Thermal parameters for α-quartz: A lattice-dynamical calculation. Acta Crystallographica, B50, 544–549.

——— (1995) Thermal parameters for minerals of the olivine group: Their implication on vibrational spectra, thermodynamic functions and transferable force fields. Acta Crystallographica, B51, 721–733.

——— (1996) Atomic displacement parameters for garnets: A lattice-dynamical evaluation. Acta Crystallographica, B52, 239–250.

Price, G.D., Parker, S.C., and Leslie, M. (1987) The lattice dynamics of forsterite. Mineralogical Magazine, 51, 157–170.

Rao, K.R., Chaplot, S.L., Choudhury, L., Ghose, S., Hastings, J.M., and Corliss, L.M. (1988) Lattice dynamics and inelastic neutron scattering from forsterite, Mg_2SiO_4: Phonon dispersion relation, density of states and specific heat. Physics and Chemistry of Minerals, 16, 83–97.

Sawada, H. (1993) The crystal structure of garnets (I): The residual electron density distribution in pyrope. Zeitschrift für Kristallographie, 203, 41–48.

Scheringer, C. (1972) A lattice-dynamical treatment of the thermal motion bond length correction. Acta Crystallographica, A28, 616–619.

Schomaker, V., and Trueblood, K.N. (1968) On the rigid-body motion of molecules in crystals. Acta Crystallographica, B24, 63–76.

——— (1984) Correlation of internal vibrational motion with overall molecular motion. Acta Crystallographica, A40 (suppl.), C339.

Smith, J.V., Artioli, G., and Kvick, Å. (1986) Low albite, $NaAlSi_3O_8$: Neutron diffraction study of crystal structure at 13 K. American Mineralogist, 71, 727–733.

Spackman, M.A., Stewart, R.F., and Le Page, Y. (1981) Maps of electrostatic properties from X-ray data for α-$SiO_{2(s)}$ and $Al_2O_{3(s)}$. Acta Crystallographica, A37, C138.

Stebler, M., Ludi, A., and Bürgi, H.B. (1986) [(phen)$_2$Mn(IV)(μ-O)$_2$Mn(III)(phen)$_2$](PF$_6$)$_3$·CH$_3$CN   and   [(phen)$_2$Mn(IV)(μ-O)$_2$Mn(IV)(phen)$_2$](ClO$_4$)$_4$·CH$_3$CN (phen = 1,10-phenanthroline): Crystal structure analyses at 100 K: Interpretation of disorder, and optical, magnetic, and electrochemical results. Inorganic Chemistry, 25, 4743–4750.

Stebler, M., and Bürgi, H.B. (1987) Dynamic processes in crystals examined through difference displacement parameters ΔU: Pseudo-Jahn-Teller distortion in cis-Cu(II)N$_4$O$_2$ coordination octahedra. Journal of the American Chemical Society, 109, 1395–1401.

Stewart, R.F. (1976) Electron population analysis with rigid pseudoatoms. Acta Crystallographica, A32, 565–574.

Trueblood, K.N. (1978) Analysis of molecular motion with allowance for intramolecular torsion. Acta Crystallographica, A34, 950–954.

Willis, B.T.M., and Pryor, A.W. (1975) Thermal vibrations in crystallography, 280 p. Cambridge University Press, U.K.

Winkler, B., Dove, M.T., and Leslie, M. (1991) Static lattice energy minimization and lattice dynamics calculations on aluminosilicate minerals. American Mineralogist, 76, 313–331.

Zulumyan, N.O., Mirgorodskii, A.P., Pavinich, V.F., and Lazarev, A.N. (1976) Study of calculation of the vibrational spectrum of a crystal with complex polyatomic anions: Diopside $CaMgSi_2O_6$. Optika i Spektroskopiya, 41, 1056–1064.