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Lattice-Dynamical Estimation of Atomic Thermal Parameters for Silicates: Forsterite α-Mg_2SiO_4

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Abstract

As an example of extending harmonic lattice-dynamical procedures to silicates, the atomic thermal parameters for forsterite Mg_2SiO_4, an important constituent of earth's crust, have been calculated on this basis. For this purpose, Iishi's rigid-ion model [*Am. Mineral.* (1978), **63**, 1190–1197; 1198–1208] was used, with slight modifications. Although such potentials were derived exclusively from fitting IR and Raman-active frequencies, the reproduction of the phonon-dispersion curves is good, and the calculation of thermodynamic functions such as entropy provides values which are near to calorimetric estimates. The calculated atomic thermal parameters are in good agreement with the experimental values reported by most authors. The calculations at various temperatures show the effect of zero-point motion very clearly: its contribution to temperature factors is about half of the total at room temperature. Bond-length corrections for thermal libration can be applied using the general-case formula: these amount to 0·003 Å for the Si—O bonds at room temperature. Although the thermal parameters in the SiO_4 group fit a rigid-body model, the correction obtained using the Schomaker–Trueblood procedure gives a significantly different result: this is essentially due to the weak librational character of the motion of silicate groups in the structure.

Introduction

The importance of atomic thermal parameters has been essentially discovered only recently; too often in fact they have been only considered as a substantial number of additional degrees of freedom to improve the final fit in least-squares refinements of crystal structures.

The first application of crystallographic thermal parameters to the problem of bond-distance correction was suggested by Cruickshank (1956) as a fit of

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such parameters to a rigid-body scheme; later on, fundamental contributions to this problem were made by Busing & Levy (1957, 1964), Schomaker & Trueblood (1968, 1984), Johnson (1969, 1970, 1980), Dunitz & White (1973), Trueblood (1978) and Trueblood & Dunitz (1983). From these results, evidence in favour of the physical meaning of the displacement parameters (or a.d.p.'s) began to be clear. On similar grounds, the so-called 'rigid-bond test' (Hirshfeld, 1976; Rosenfield, Trueblood & Dunitz, 1978) has been shown to hold almost universally, and for the few cases where discrepancies are observed there are precise physical reasons [see, for instance, Bürgi & Dunitz (1983)].

An independent verification of the physical validity of the crystallographic a.d.p.'s can be obtained from lattice dynamics. For structures of moderate complexity the best results have been obtained for molecular crystals. Here, in fact, the rigid-body model can be assumed to hold in many cases, and for less simple molecules a limited number of internal degrees of freedom can be considered to couple with the lattice motion. The first practical examples of these calculations with the rigid-body model have been shown by Cochran & Pawley (1964) to evaluate the diffuse scattering of hexamethylenetetramine, by developing the ideas of Born (1942) and Laval (1941). Further significant applications were reported by Pawley (1967, 1968), who explained in detail the relationships between the lattice-dynamical formulation and the crystallographic procedure; some useful theoretical contributions to the point are given by Scheringer (1972), Willis & Pryor (1975), and other authors. The extension of the rigid-body treatment to non-rigid molecules including the lowest internal frequencies was first proposed by Bonadeo & Burgos (1982) for biphenyl crystals; a procedure for the general case was given by Gramaccioli & Filippini (1983) with examples concerning a series of aromatic hydrocarbons of increasing complexity and non-rigidity. For charged molecules, a first example of such a calculation was given recently by Criado (1990); further details and references concerning the development of these ideas and routines can be found, for instance, in Gramaccioli (1987). For most of the cases considered so far, there is a good to excellent agreement between the results of lattice-dynamical calculations and the experimental values of the a.d.p.'s; when the agreement is poor, as for instance for benzene at relatively high temperature (138 K), the discrepancy can be ascribed to clear physical reasons [see, for instance, Filippini, Gramaccioli, Simonetta & Suffritti (1974) and Filippini & Gramaccioli (1989)].

Whereas, as we have seen, there are already a substantial number of examples in the literature of lattice-dynamical evaluations of a.d.p.'s for organic molecular crystals, there are practically no examples of calculations of this kind for minerals or inorganic substances in general. The few exceptions are sophisticated treatments of simple structures, such as sodium or potassium chloride [see, for instance, Reid & Smith (1970)] or cases like sulfur (Rinaldi & Pawley, 1973, 1975; Gramaccioli & Filippini, 1984), which is, however, still a molecular crystal.

All this is in spite of high interest in possible geological applications, especially for silicates, or also in materials science applications: here the interest goes far beyond the possibility of calculating the a.d.p.'s, since it involves the possibility of evaluating the elasticity coefficients, and especially thermodynamic functions starting from crystal-structure data. Among the latter, a lattice-dynamical treatment permits the evaluation of specific heats c_v and c_p, and also the vibrational contribution to functions involving the second law, such as entropy S and free energy F. The solution of such a problem would emphasize the fundamental role of crystallography, not only for knowing how a certain mineral is formed, but also for deducing its behaviour under different conditions, a question which is regarded as much more important and interesting by petrologists and geologists in general [see, for instance, Kieffer & Navrotski (1985)].

Since it is necessary to perform a complete lattice-dynamical sampling of the Brillouin zone in order to obtain the a.d.p.'s, this difficult and lengthy operation also permits thermodynamic functions to be deduced with very little additional effort.

Why are such examples so few in the literature? The main difficulties with these substances can be ascribed to several factors: (1) the presence of charged atoms; (2) the absence (in general) of definite molecular units of limited extension; (3) the virtual lack of well-checked potentials which can be safely applied to a sufficiently wide group of minerals; and (4) the difficulties in obtaining reliable experimental data, *e.g.* a.d.p.'s that are not suffering significantly from absorption or especially extinction; also spectroscopic data (IR, Raman) are not always reliable, the interpretation and/or the symmetry labelling being questionable in most cases, and there is no information concerning phonon-dispersion curves, except for a limited number of substances.

The presence of charge makes evaluation of the lattice sums difficult because of very slow convergence: if a reasonable result is required, the summations should be carried on the reciprocal lattice, following a routine first derived by Ewald (1921) for the static case, and then extended to the dynamical case by Born & Thompson (1934), Thompson (1935), and for the first time in a correct form by Kellermann (1940) in his classic work on sodium chloride.

For the rigid-ion approximation or similar models, this routine has still remained essentially the same; a more general treatment of the static problem has been given by Bertaut (1952), and an extension of Bertaut's method to the dynamical problem has been developed by us quite recently (Pilati, Bianchi & Gramaccioli, 1990*a*).

The difficulty for the charge problem becomes still greater if the effects of polarizability are taken into account. Fortunately, although such effects do exist, a rigid-ion model seems to work reasonably well in the few silicates which have been considered so far, *i.e.* quartz (Elcombe, 1967; Iishi, 1976; 1978; Iishi, Miura, Shiro & Murata, 1983), forsterite (Iishi, 1978; Ghose, Hastings, Corliss, Rao, Chaplot & Choudhury, 1987; Rao, Chaplot, Choudhury, Ghose, Hastings & Corliss, 1988), andalusite (Iishi, Salje & Werneke, 1979). For forsterite, the agreement with the optical frequencies seems to be worse for a polarized-ion model than for the rigid-ion model, in spite of the more elaborate nature of the former (Iishi, 1978).

For these reasons, at least as a preliminary stage for studying the possibility of application to such compounds, we decided to adopt the rigid-ion model, using our own method for evaluating Coulombic lattice sums. For forsterite, α-Mg_2SiO_4, a member of the olivine group which can be considered as one of the simplest (and most important) silicates to deal with, the problem of absence of a definite molecular structure is probably not so evident as it is for multiple chain-, sheet- or tecto-silicates. In the olivine structure, in fact, isolated tightly bonded SiO_4 groups are present, connected by Mg ions *via* comparatively weaker Mg—O bonds of prevailing ionic character. On these grounds, the models proposed by Ghose *et al.* (1987) and Rao *et al.* (1988) have been worked out. However, in view of future extensive applications to a wide variety of compounds, we have developed a general-purpose routine which does not necessarily imply the presence of isolated (or nearly isolated) groups; some difficulties were encountered, especially in coding the bending interactions between atoms in the structure belonging to different unit cells, and this problem is particularly evident for non-zero values of the wavevector **q**.

Although the problem of adequate semi-empirical potentials is far from being solved for the general case in calculating the vibrational properties of silicates, for forsterite some reliable force fields are given in the literature. For instance, Iishi (1978) could get a very reasonable fit to the observed Raman and IR-active frequencies of this mineral by essentially applying a modified Urey–Bradley field (Shimanouchi, 1963) and by assigning an appropriate charge to the centre of the Mg, Si and O atoms (see Table 1). Another force field for forsterite which can be applied to rigid-ion models has been proposed by Rao *et al.* (1988).

Table 1. *Atomic parameters used in the present work (derived from Iishi's RI3 field by conversion of Urey–Bradley force-field parameters into valence force-field parameters)*

Charge Z (in electron units)
Mg = 0·93; Si = 0·70; O = −0·64

Stretching constants (mdyn Å^{-1})
Mg—O = 0·502 (0·64 final); Mg—Si = 0·037; Si—O = 5·298–0·59(d − 1·637)
[for Si—O d is the measured bond length (Å)]

Bending constants (mdyn Å)
O—Si—O = 1·34 − 0·022(φ − 109·17) [φ is the measured angle (°)]

Stretching-stretching of adjacent Si—O bonds (mdyn Å^{-1})
χ = 0·247

Stretching–bending of adjacent Si—O bonds and O—Si—O angles (mdyn)
ψ = 0·500 − 0·01(φ − 109·17)

Bending–bending for O—Si—O angles sharing one edge (mdyn Å)
ω = 0·12

Interactions for the van der Waals field (below 3·5 Å) between two oxygen atoms of different tetrahedra (KJ mol^{-1}), as $E = 528497r^{-9} - 34987r^{-6}$ (r is the distance in Å).

For forsterite, reliable experimental data concerning thermodynamic functions and even phonon-dispersion curves are available (Robie, Hemingway & Takei, 1982; Ghose *et al.*, 1987); in addition, several independent determinations of the a.d.p.'s by crystal structure refinement can be found in the literature both for natural and synthetic crystals (Birle, Gibbs, Moore & Smith, 1968; Hazen, 1976; Fujino, Sasaki, Takéuchi & Sadanaga, 1981; Bocchio, Brajkovic & Pilati, 1986; Langen, 1987). These are further reasons for having chosen this substance as the first silicate on which comparison between theoretical and experimental thermal parameters could be attempted.

Method of calculation

The elements of the dynamical matrix $\mathbf{D}(\mathbf{q})$ for a certain value of the wavevector $\mathbf{q}$ are given by

$$D_{ij}^{pp'}(\mathbf{q}) = (m_p m_{p'})^{-1/2} \textstyle\sum_l \Phi_{ij}^{pp'}(0,l)\exp(2\pi i\mathbf{q}.\Delta\mathbf{x}^l) \quad (1a)$$

with

$$\Phi_{ij}^{pp'}(0,l) = \partial^2 E / \partial x_{ip}^0 \partial x_{jp'}^l \quad (1b)$$

[see, for instance, Willis & Pryor (1975), equation 3.10*b*], where E is the energy of interaction between the atoms p and p', x_{ip}^0 is a coordinate of the pth atom in the unit cell, $x_{jp'}^l$ is a coordinate of the p'th atom in the crystal, related to $x_{jp'}^0$ by the lattice translation $\mathbf{r}^l$, $\mathbf{q}$ is the wavevector, $\Delta\mathbf{x}^l$ is the distance between the two atoms involved, and m_p and $m_{p'}$ are the masses of the respective atoms. The summation $\sum_l$ is extended (in principle) over the entire crystal.

By diagonalizing $\mathbf{D}(\mathbf{q})$ the normal-mode frequencies $\nu_\psi(\mathbf{q})$ are obtained (in the harmonic approximation); for a certain ψ mode relative to a certain value of $\mathbf{q}$ the average energy $E_\psi(\mathbf{q})$ can be obtained as

$$E_\psi(\mathbf{q}) = h\nu_\psi(\mathbf{q})(1/2 + \{\exp[h\nu_\psi(\mathbf{q})/kT] - 1\}^{-1}) \qquad (2)$$

where h and k are the Planck and the Boltzmann constants, respectively, and T is the absolute temperature. From these data and the mass-adjusted polarization vectors $\mathbf{e}(p|\psi\mathbf{q})$ of the atoms in the unit cell, which are part of the eigenvectors of the $\mathbf{D}(\mathbf{q})$'s, the a.d.p.'s [as $\mathbf{U}(p)$'s] can be obtained as

$$\begin{aligned}\mathbf{U}(p) = {} & (Nm_p)^{-1}\textstyle\sum_{\psi,\mathbf{q}}E_\psi(\mathbf{q})[2\pi\nu_\psi(\mathbf{q})]^{-2} \\ & \times \mathbf{e}(p|\psi\mathbf{q})[\mathbf{e}^*(p|\psi\mathbf{q})]' \qquad (3)\end{aligned}$$

where N is the total number of unit cells in the crystal.

Similarly, thermodynamic functions such as the molar heats c_v and c_p as well as the entropy S can be derived from the same data:

$$\begin{aligned}c_v = {} & 3R\textstyle\sum_\nu g_\nu (h\nu/kT)^2\exp(h\nu/kT) \\ & \times[\exp(h\nu/kT) - 1]^{-2}\Delta\nu \qquad (4a)\end{aligned}$$

$$c_p = c_v + \beta^2 TVK_T \qquad (4b)$$

$$S = E_{\rm vib}/T - 3R\textstyle\sum_\nu g_\nu \ln[1 - \exp(h\nu/kT)]\Delta\nu. \qquad (4c)$$

Here $E_{\rm vib}$ is the vibrational energy of the crystal, and g_ν is a density-of-states function, normalized to $\sum_\nu g_\nu \Delta\nu = 1$. In (4*b*) β is the coefficient of volume expansion and K_T is the isothermal bulk modulus: in this work (see below) the experimental data for these two quantities quoted by Price, Parker & Leslie (1987) have been used.

The summations are extended to all the vibrational modes (ψ) for a certain point of the Brillouin zone and (in principle) to all the points in the Brillouin zone, each of them corresponding to a certain value of the wavevector $\mathbf{q}$: for details about this procedure, see for instance Willis & Pryor (1975), or Filippini, Gramaccioli, Simonetta & Suffritti (1976). An uneven sampling of the Brillouin zone turns out to be particularly useful for fast convergence to a final value, otherwise the number of points to be sampled would become too large [see, for instance, Filippini & Gramaccioli (1989) and Kroon & Vos (1978, 1979)]. In order to improve this procedure, a new set of progression formulae has been derived recently (Pilati, Bianchi & Gramaccioli, 1990*b*); the difference with respect to a very extensive sampling of the Brillouin zone (involving 10^3–10^4 points) and sampling over a considerably smaller number of points (64), as we have used here, is small (about 1–2% for the B's and less than 0·2% for entropy), owing to the fast convergence of the series adopted here.

The second derivatives in (1*b*) of the interaction energy have been evaluated analytically by considering the interaction energy to be a sum of various contributions, *i.e.* the modified Urey–Bradley force field (including the van der Waals field) and the Coulombic contribution. For the former, the parameters proposed by Iishi (1978) in his Table 4 for his rigid-ion model *RI*3 have been used initially, and Simanouti's (1949) routine has been employed for deducing stretching, bending and interaction constants: these data are reported in Table 1. Of the parameters reported in Iishi's table, only one called p and described as 'bond interaction for SiO_4 internal modes', or also as 'bond–bond interaction for the adjacent Si—O bond pairs' (Iishi, 1978) does not seem to match the subsequent Simanouti treatment. For this reason we have chosen the value $p = 0{\cdot}144$ (instead of 0·288) on the basis of best fit with respect to Raman and IR frequencies. The van der Waals interactions have been considered for O—O contacts up to 3·5 Å in length.

The Coulombic contributions to the dynamical matrices $\mathbf{D}(\mathbf{q})$ have been evaluated by the modification of Bertaut's method recently developed by us (Pilati *et al.*, 1990*a*): the atomic charge values are those proposed by Iishi (1978) for his rigid-ion model. Our modification of Bertaut's method, which replaces Ewald's routine, works in terms of second derivatives of structure factors, where the atomic form factors are replaced by the corresponding charge, and is close to usual crystallographic calculations. The advantages of this procedure are its simplicity and the implicit accounting for the contributions of the macroscopic field, leading to TO–LO splitting for IR-active modes. In this application the reflections up a maximum $\sin\theta/\lambda$ value of 0·5 Å^{-1} have been considered.

Results and discussion

Our calculated values for the frequencies at $\mathbf{q} = 0$ are reported in columns 4 and 5 of Table 2, which also gives the corresponding results and experimental values from Iishi (1978), Price *et al.* (1987) and Rao *et al.* (1988).

The difference between our results in column 4 and Iishi's are essentially small, as indeed they should be, since the same force field has been used, with the exception of the interpretation of the p parameter, as stated above.

Notwithstanding the limitations of the rigid-ion model, Iishi's fit to his experimental data is apparently the best: this good agreement of Iishi's *RI*3 model is a significant point in its favour, although it derives in part from the fact that the parameters have been specifically adjusted to provide the best fit to these frequencies; the number of such parameters

Table 2. *Observed and calculated frequencies* (cm^{-1}) *for forsterite at the* Γ*-point* ($\mathbf{q} = 0$) (*our calculations with* Mg—O *stretching force constant of* 0·502 *or* 0·702 mdyn Å^{-1}, *respectively*)

In the first column the range of observations by the different authors is reported. For IR-active modes, the range includes TO–LO splitting: for simplicity, Iishi's observed values are only reported here if they are considerably different from the other values.

	Obs.	Iishi obs.	Iishi calc.	Our 0·502	Our 0·702	Price	Rao obs.	Rao calc.
A_g	960–966	966	958	955	959	943		
	854–856	888	888	893	896	851		
Γ_1	822–826	826	837	835	841	807		
	606–609	609	606	635	659	630		
	541–545	546	535	549	566	580		
	420–424	424	414	464	504	427		
	334–340	340	358	334	374	360		380
	325–329	329	287	299	344	344		342
	304–305	305	269	256	295	312		293
	221–227	227	228	218	227	221		252
	181–183	183	157	175	193	184		178
A_u				907	910	938		
				526	551	519		
Γ_2				501	528	479		
				359	404	452		458
				329	381	391		403
				298	353	340		359
				264	310	271		286
				223	262	250		233
				184	200	166		170
				130	138	58	104	105
B_{1g}	917–922	922	894	909	911	960		
(B_{3g})	588–595	595	580	580	596	606		
	407–412	412	411	464	492	417		
Γ_3	371–376	376	367	348	387	390		382
	312–318	318	304	299	333	327		328
	272	272	277	261	308	250		256
	226	226	234	237	257	133		174
B_{2g}	972–976	976	961	956	961	963		
(B_{1g})	863–866	866	891	895	898	864		
	835–839	839	846	838	845	821		
Γ_4	626–632	632	629	645	667	667		
	577–583	583	583	569	592	617		
	428–434	434	412	473	503	454		
	418	418	396	355	403	428		517
	314–318	318	316	316	349	337		367
	260–265	260	276	274	303	325		321
	215–224	224	230	226	247	269		264
	149 192	192	180	188	210	231		223
B_{3g}	880–884	884	891	902	905	901		
(B_{2g})	583–588	588	591	582	595	611		
	436–441	441	451	479	514	433		
Γ_5	354–368	368	362	371	415	365		452
	324	324	306	287	331	345		314
	237–244	244	267	256	284	207		288
	142–150	142	166	152	162	149		
B_{1u}	980–1086		956–976	954–974	959–979	995–1084		
(B_{3u})	957–963		915–916	913–913	916–916	960–991		
	838–845		826–827	836–836	842–842	812–815		
Γ_6	601–645		565–601	615–638	638–667	657–658		
	562–566		527–527	546–546	574–574	573–638		
	498–544		493–494	514–514	548–548	520–571		
	438–469	—	—	—		482–516		
	403–438	403–469	403–413	368–398	421–436	437–471		531–601
	378–386		362–392	352–366	399–419	376–394		457–531
	320–323		312–347	305–337	347–376	349–349		416–441
	293–298		303–309	293–302	332–332	307–313		364–414
	274–276		264–265	261–261	289–290	293–293		321–356
	(224)	224	238–242	227–229	256–257	—		300–315
	201		188–190	156–157	173–174	193–197		132–135
B_{2u}	885–994		890–913	902–923	904–926	879–1028		
(B_{3u})	502–585		492–540	528–564	549–590	513–598		
	483–489		480–491	510–510	544–547	476–452		
Γ_7	423–459		417–420	384–389	435–442	450–475		414–618
	365–371		345–362	318–353	375–388	375–390		389–413
	296–318		309–343	289–316	345–369	347–362		323–339
	274–278		266–274	242–253	278–287	313–321		293–300
	274		230–231	219–219	250–251	250–251		276–279
	201		208–209	188–188	204–204	176–177		202–204
B_{3u}	987–993		957–958	956–956	960–960	958–959		
(B_{2u})	882–979		897–917	892–913	895–916	900–906		
	838–843		833–833	838–838	845–845	834–834		
Γ_8	—	—	—	—	625–625	647–647		
	537–597		581–584	535–564	565–591	581–581		
	510–516		543–560	512–541	535–554	542–543		
	465–493		467–513	—	—	467–479		
	421–446		417–423	367–376	411–421	427–430		562–624
	400–412		357–359	344–355	394–397	364–364		485–561
	352–376		321–344	305–341	359–384	338–354		408–480
	294–313		314–317	295–296	336–336	280–284		381–403
	280–283		278–297	266–281	300–311	250–250		312–332
	244	224	235–238	238–242	272–279	—		267–267
	144		139–140	161–161	137–138		201	193–194

(14) is comparable with the models of Price *et al.* (13 parameters) and Rao *et al.* (14 parameters for their molecular-ion model and 19 for their rigid-ion model). However, the model of Price *et al.* has been derived, at least in part, from fitting other properties (not necessarily only the IR and Raman-active frequencies) and from Hartree–Fock *ab initio* calculations. Similarly, some of the parameters of Rao *et al.* seem to have been derived not particularly for forsterite, and here the agreement with further (nonspectroscopic) data, such as elastic constants, *etc.* has been considered as well. Probably the best appreciation of these more recent models will be obtained if they are extended to a sufficiently large group of different minerals.

Fig. 1 reports the calculated phonon-dispersion curves with our interpretation of Iishi's *RI*3 field; they are compared with the experimental values obtained by Ghose *et al.* (1987). Although no fit to such data was ever considered by Iishi (since no experimental data of this kind were available at that time and no calculations for $\mathbf{q} \neq 0$ were performed by him), his *RI*3 field behaves well in predicting the phonon-dispersion curves* and therefore probably has some intrinsic physical validity. In considering such a fit, particular importance should be given in our case to the lowest frequencies, since the calculated values of the **U**'s (or **B**'s) depend almost exclusively on them.

In view of this situation, a slight adjustment of Iishi's field seemed reasonable. In fact, some calculated branches (see Σ_3 and Δ_1 in Fig. 2) are appreciably too low with respect to the experiment, and here the model of Rao *et al.* appears to be much better, in spite of the poor agreement with the Raman and IR data (however, some of the low-frequency Raman and IR experimental data are rather questionable, in spite of their importance for

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* For a very small region of the Brillouin zone in the proximity of the origin and centred on $\mathbf{q} = (0·003, 0·003, 0·003)$ there are imaginary frequencies of the order of $2\text{–}3i$ (cm^{-1}). In this case our calculations have been performed by assuming the lowest acoustic branch to be a straight line in that interval.

our purposes). Another indication that especially the lowest frequencies are calculated too low is the estimated value of the entropy at 298 K (= 103·0 J mol^{-1} K^{-1}), which is too large with respect to the experimental result [94·03 J mol^{-1} K^{-1} in Robie *et al.* (1982)].

A reasonable proposal might be to raise some of the calculated branches, especially the acoustic ones in the low-frequency region: here, the Mg—O contacts should dominate the situation, since they correspond to the weakest points in the structure.

For this reason, we have tried to harden the Mg—O bonds, by raising the corresponding stretching force constant to 0·702 mdyn Å^{-1} (no satisfactory result was obtained on varying the atomic charge). Using this 'new' field, we have re-calculated all Raman and IR-active frequencies, and the results are reported in the column 5 of Table 2. Whereas the fit to some of the higher frequencies is slightly worse, for the lowest frequencies, and especially in the lowest part of the acoustic branches, there is a slight but definite improvement (see Fig. 2); the situation is still better than it appears in the drawing, since other values measured by different authors and reported in Table 2 for **q** = 0 are nearer to our calculations than the data of Ghose *et al.* (1987). Also, the calculated value of entropy (91·4 J mol^{-1} K^{-1}) at room temperature is consistent with the experimental value. If the stretching constant of the Mg—O bonds is further increased, the improvement becomes less evident.

In order to have the best agreement with the experimental data, we finally adjusted the value of the Mg—O stretching constant to match the experimental value for entropy at room temperature (298 K): this corresponds to a value of 0·64 mdyn Å^{-1}.

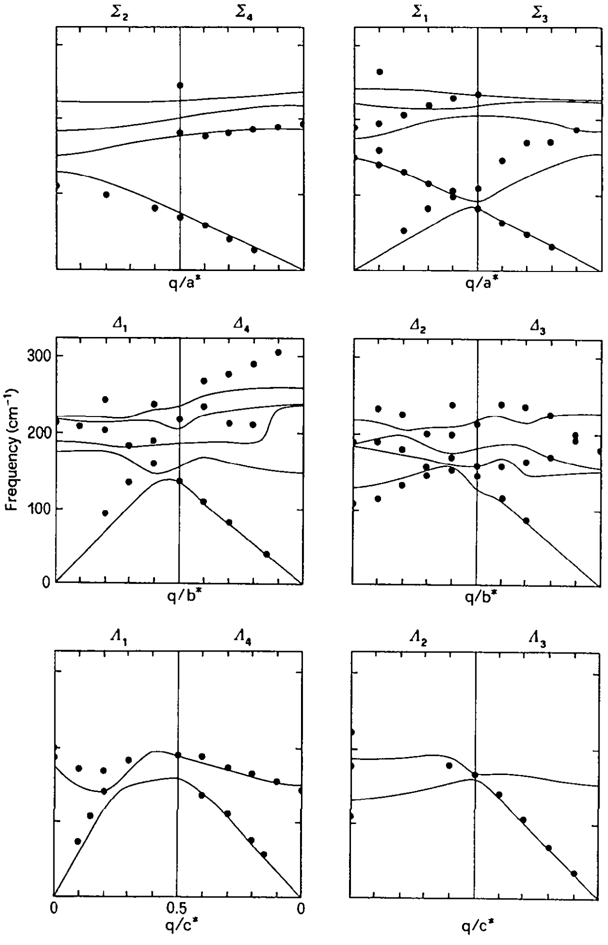

Fig. 1. Calculated phonon-dispersion curves for forsterite along the crystal axes *a*, *b* and *c*. Here a stretching constant of 0·502 mdyn Å^{-1} for the Mg—O bonds has been used, as in Iishi's *RI*3 field; the points correspond to the experimental values obtained by Ghose *et al.* (1987) and these values only are reported. For simplicity, the higher curves are not represented in the drawing.

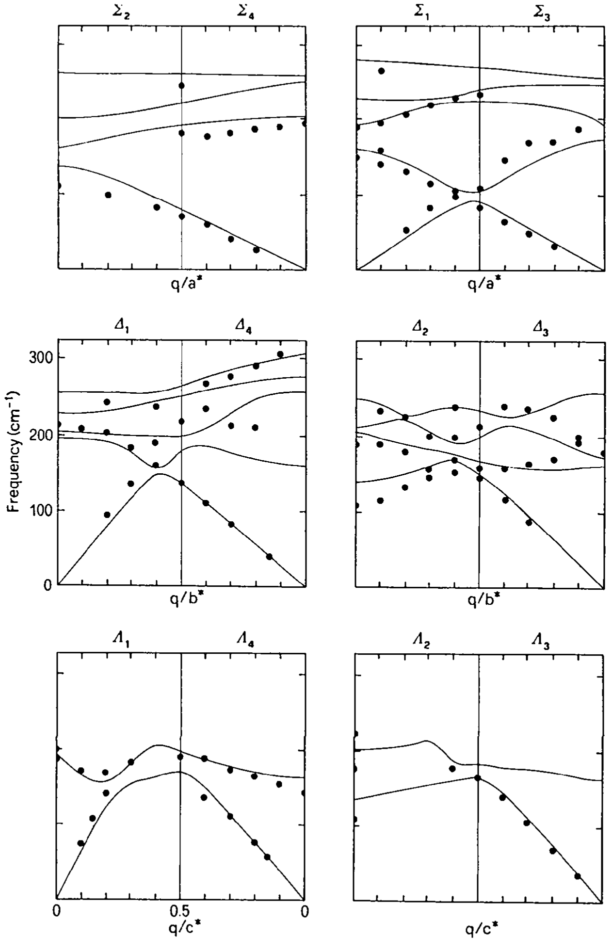

Fig. 2. Calculated phonon-dispersion curves for forsterite. The situation is the same as for Fig. 1 with the exception of the Mg—O stretching constant, which has been raised to 0·702 mdyn Å^{-1}.

Table 3. *Calculated anisotropic atomic displacement parameters* ($\times 10^5$) *for forsterite at various temperatures*

The temperature factor is in the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{23}klb^*c^*)]$. The cell parameters in our reference system are chosen so that $a > b > c$; the atomic coordinates correspond to Fujino *et al.* (1981) with the exception of O(2), which is transformed by $1/2 + x$, y, $1/2 - z$.

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	U_{eq} (Å^2)
$T = 0$ K (zero-point contribution)							
Mg(1)	297	−25	−14	260	−16	263	273
Mg(2)	253	0	12	274	0	272	266
Si	171	0	3	166	0	143	160
O(1)	299	0	0	298	0	183	260
O(2)	212	0	−12	296	0	260	256
O(3)	284	41	17	235	−6	256	258
$T = 20$ K							
Mg(1)	298	−25	−14	261	−16	264	274
Mg(2)	254	0	12	275	0	272	267
Si	172	0	3	168	0	144	161
O(1)	300	0	0	299	0	183	261
O(2)	213	0	−12	297	0	260	257
O(3)	285	41	17	236	−6	257	259
$T = 77$ K							
Mg(1)	329	−29	−16	284	−18	281	298
Mg(2)	276	0	13	297	0	290	288
Si	194	0	3	187	0	157	179
O(1)	323	0	0	320	0	196	280
O(2)	234	0	−12	316	0	274	275
O(3)	307	42	18	255	−5	271	278
$T = 298$ K							
Mg(1)	707	−88	−44	566	−52	544	606
Mg(2)	538	0	39	596	0	570	568
Si	400	0	9	383	0	292	358
O(1)	581	0	1	568	0	319	489
O(2)	421	0	−7	554	0	454	476
O(3)	553	78	34	452	6	446	484
$T = 453$ K							
Mg(1)	1028	−133	−67	815	−79	781	875
Mg(2)	773	0	59	861	0	820	818
Si	574	0	13	548	0	410	511
O(1)	817	0	2	797	0	429	681
O(2)	583	0	−8	776	0	626	662
O(3)	775	115	50	628	12	614	672
$T = 578$ K							
Mg(1)	1306	−173	−80	1048	−102	989	1114
Mg(2)	978	0	77	1106	0	1043	1042
Si	731	0	17	710	0	523	655
O(1)	1036	0	3	1027	0	538	867
O(2)	733	0	−12	1002	0	794	843
O(3)	985	148	66	804	13	779	856
$T = 723$ K							
Mg(1)	1612	−217	−100	1293	−127	1224	1376
Mg(2)	1201	0	96	1362	0	1292	1285
Si	896	0	22	873	0	644	804
O(1)	1272	0	4	1266	0	655	1064
O(2)	891	0	−15	1234	0	976	1034
O(3)	1207	185	82	981	16	958	1049
$T = 883$ K							
Mg(1)	1955	−267	−122	1567	−156	1487	1670
Mg(2)	1450	0	117	1649	0	1572	1557
Si	1082	0	26	1056	0	783	974
O(1)	1539	0	4	1537	0	791	1289
O(2)	1070	0	−20	1498	0	1186	1251
O(3)	1461	227	100	1182	19	1165	1269
$T = 1023$ K							
Mg(1)	2269	−311	−146	1810	−180	1722	1934
Mg(2)	1680	0	135	1903	0	1821	1801
Si	1258	0	28	1219	0	908	1128
O(1)	1790	0	4	1779	0	915	1495
O(2)	1240	0	−26	1734	0	1374	1449
O(3)	1698	263	115	1362	21	1352	1471
$T = 1173$ K							
Mg(1)	2587	−359	−167	2071	−207	1973	2210
Mg(2)	1909	0	154	2174	0	2088	2057
Si	1433	0	32	1395	0	1043	1290
O(1)	2048	0	4	2047	0	1047	1714
O(2)	1410	0	−32	1995	0	1580	1662
O(3)	1942	304	132	1556	23	1554	1684
$T = 1293$ K							
Mg(1)	2830	−398	−183	2279	−228	2173	2427
Mg(2)	2079	0	169	2392	0	2303	2258
Si	1557	0	34	1536	0	1154	1416
O(1)	2238	0	4	2261	0	1157	1885
O(2)	1530	0	−39	2204	0	1750	1828
O(3)	2122	335	146	1711	22	1723	1852

The calculated a.d.p.'s as **U**'s or U_{eq}'s at room temperature (298 K) are reported in Table 3; these can be compared with the experimental results obtained by a few authors, who refined the structure of forsterite with particular care, such as for instance Birle *et al.* (1968), Hazen (1976), Fujino *et al.* (1981), Bocchio *et al.* (1986) and Langen (1987) (see Table 4). The agreement is remarkably good, especially in view of theoretical and experimental difficulties. Hazen's results are exceptional, all being too low, not only with respect to our calculations, but also with respect to all the other experimental values. Moreover, at low temperature (77 K) Hazen's experimental values for all the **U**'s are non-positive definite. Therefore, in Hazen's work there is a serious drawback concerning the magnitude of the a.d.p.'s, which are too low: as it is suggested in a footnote of the article itself, this fact is very probably due to a particularly strong extinction, because a highly perfect, gem-quality synthetic crystal was used, and no general correction for extinction was made (only some of the strongest reflections were discarded from the refinement). In Fujino *et al.* (1981), which is probably the most accurate structural work in view of electron-density measurement, the data were also obtained from a synthetic crystal, but extinction was accounted for according to Zachariasen's (1967) method. For all the other forsterite samples, natural crystals were used, most of which came from a rock's bulk, and were therefore not necessarily perfect, although single. The purity of these natural forsterites is nearly exactly 90%, the rest being almost exclusively the corresponding iron compound α-Fe_2SiO_4 (fayalite). In order to check whether the presence of iron influences the values of the a.d.p.'s, our calculations have been repeated by assuming the mass of the metal atoms to be the weighted average of Mg and Fe; the results are practically identical (within 1%), and the differences are well below the presumable accuracy of the experimental data (10–20% for the diagonal terms). Also the experimental values of the **U**'s for other terms of the olivine series rich in iron, up to fayalite itself, are not substantially different from those of forsterite [see Birle *et al.* (1968) and Fujino *et al.* (1981): there is only a slight increase up to 10–20% for the pure end member].

Table 4. *Anisotropic atomic displacement parameters* ($\times 10^5$) *for forsterite at room temperature, from crystal structure refinement*

The reference system and the expression of temperature factors are the same as for Table 3. The standard deviations in the data are 10^{-4} to 3×10^{-4} (Bocchio *et al.*), 3×10^{-4} to 8×10^{-4} (Hazen), about 5×10^{-5} (Langen), 10^{-4} to 2×10^{-4} (Fujino *et al.*), and about 5×10^{-4} (Birle *et al.*), all in Å^2.

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	U_{eq}(Å^2)
Langen (1987), model *G* (high-order reflections)							
Mg(1)	702	−110	−10	469	−59	450	540
Mg(2)	466	0	15	547	0	590	534
Si	415	0	14	405	0	286	369
O(1)	699	0	36	576	0	315	530
O(2)	421	0	5	607	0	526	518
O(3)	677	163	31	523	−26	515	572
Bocchio *et al.* (1986) (crystal *PB*9, high-order reflections)							
Mg(1)	578	−118	0	575	−69	539	564
Mg(2)	339	0	17	635	0	692	555
Si	292	0	15	500	0	381	391
O(1)	573	0	−42	644	0	400	539
O(2)	329	0	−10	702	0	589	540
O(3)	530	149	30	630	−32	599	586
Hazen (1976) (data at 296 K and 1 atm)							
Mg(1)	540	−93	20	180	−40	280	333
Mg(2)	320	0	0	290	0	250	289
Si	230	0	12	150	0	90	157
O(1)	480	0	50	420	0	100	333
O(2)	370	0	−20	400	0	280	350
O(3)	490	120	20	290	−40	250	343
Fujino *et al.* (1981)							
Mg(1)	710	−111	−15	512	−55	477	566
Mg(2)	490	0	22	596	0	592	560
Si	437	0	2	422	0	300	385
O(1)	620	0	10	560	0	340	508
O(2)	430	0	10	600	0	500	510
O(3)	630	148	15	510	−27	510	551
Birle *et al.* (1968)							
Mg(1)							418
Mg(2)							456
Si							253
O(1)							443
O(2)							532
O(3)							519

The lattice-dynamical calculations clearly account for the comparatively low U_{eq} value for Si, which was about two-thirds of the corresponding values for Mg and O atoms: this situation has already been noted by Burnham (1965) in the experimental values for many other silicates, and is a consequence of strong bonds between oxygen and four-valent silicon. Also the anisotropic behaviour of the a.d.p.'s is substantially well reproduced: the components of the **U** (and **B**) tensors are in agreement with their experimental values even for O(1), where anisotropy is *particularly marked* (*U_{33} is about half of either* U_{11} or U_{22}). In order to give a pictorial representation of the agreement of our theoretical results with the experimental data, *ORTEP*II drawings (Johnson, 1976) of the asymmetric unit of forsterite at room temperature including thermal ellipsoids are given in Fig. 3.

In view of this favourable situation, we have repeated the calculations for different values of temperature, and Table 3 reports our results for a comparison and further check of this model with future accurate experimental work. For this purpose Hazen's unit-cell parameters have been used, since they agree with the corresponding data from other authors, when available; for very low temperatures the same unit-cell parameters as for 77 K were used, because of the lack of experimental data and also because, on the other hand, the unit-cell parameters undergo only a minor change with temperature, so that no significant influence on our calculations can be expected. Table 3 also shows the variation of the equivalent isotropic *U*'s as a function of temperature: for the lowest values of *T*, the situation is very different from all too many plots which are reported in the literature, where extrapolation to zero for $T \rightarrow 0$ is assumed. Here, and especially for such strongly bonded structures as silicates, the relative importance of the zero-point contribution is quite *large* and corresponds to about half of the total at room temperature; a similar situation (although less marked, because the structure is molecular, and therefore less strongly bonded) was pointed out recently by Filippini & Gramaccioli (1989) for benzene crystals.

The plot of the calculated *U*'s *versus* temperature could be extended towards high values of *T*; however, beyond a certain point the harmonic approximation might not hold, and for this reason we did not extend our calculations above 1300 K.

Besides examining temperature factors, a consistent check might be examining some thermodynamic functions as well, such as for instance entropy *S* and the molar heat c_p (see Table 5). The agreement with the experimental values of Robie *et al.* (1982) is quite reasonable, and this confirms our good grounds for being confident in our predictions of the a.d.p.'s in this temperature range. At very low temperature, the difference between the observed and calculated values of the thermodynamic functions, which drop to zero in the proximity of 0 K, becomes considerable on a *relative* basis; in this respect, the

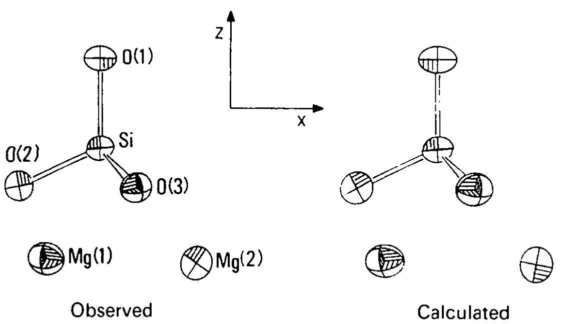

Fig. 3. An *ORTEP*II drawing (projection on the mirror plane {010}) of the calculated and observed (Bocchio *et al.*, 1986) thermal ellipsoids for the asymmetric unit of forsterite at room temperature. The volume of the ellipsoids corresponds to a 99·9% probability.

Table 5. *Observed and calculated* c_p *and* S (J mol^{-1} K^{-1}) *for forsterite at various temperatures* (K)

The experimental data are from Robie *et al.* (1982).

T	c_p(obs)	c_p(calc)	*S*(obs)	*S*(calc)
20	0·27	0·31	0·08	0·02
77	18·64	19·21	6·72	6·50
298	118·5	118·4	94·0	94·0
453	143·3	145·6	148·9	148·3
578	154·1	157·4	185·5	185·0
723	162·9	165·6	221·2	220·2
883	170·5	171·5	254·6	252·9
1023	176·0	175·1	280·4	277·5
1173	180·7	178·1	304·5	300·8
1293	183·9	180·2	322·4	317·6

results obtained by Price *et al.* (1987) using a more sophisticated (shell) model are definitely better. However, for all the other temperatures (which correspond to the most usual conditions) the rigid-ion model behaves very satisfactorily, in spite of its simpler nature.

The normalized density of states for forsterite according to our calculations is shown in Fig. 4. In this respect, the only comparison which can be made is with the calculations of Price *et al.* (1987) and Rao, Chaplot, Choudhury, Ghose & Price (1987). All agree on the gap between 650 and 800 cm^{-1} corresponding to separation between the high-frequency stretching modes of the Si—O bonds and the lower frequency modes. We have, however, another smaller gap around 450 cm^{-1}, corresponding grossly to the separation between the bending modes of the SiO_4 tetrahedra and the 'lattice' modes mainly involving Mg—O stretching.

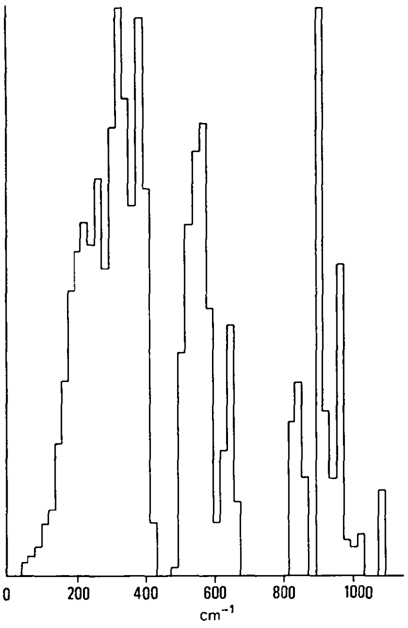

Fig. 4. Density of states histogram for forsterite, from our calculations.

Table 6. *Values of the* Si—O *distances* (Å) *as a function of temperature*

The experimental data are taken from Hazen (1976). The correction for thermal libration derives from our lattice-dynamical calculations.

	Si—O(1)		Si—O(2)		Si—O(3)	
T (K)	Uncorr.	Corr.	Uncorr.	Corr.	Uncorr.	Corr.
77	1·616 (2)	1·618	1·649 (2)	1·651	1·633 (2)	1·635
296	1·615 (3)	1·618	1·640 (3)	1·643	1·633 (2)	1·636
623	1·614 (3)	1·618	1·636 (4)	1·640	1·624 (3)	1·628
1047	1·615 (5)	1·622	1·636 (5)	1·643	1·623 (3)	1·630
1273	1·615 (4)	1·625	1·649 (4)	1·659	1·628 (3)	1·638

Since lattice dynamics provides not only thermal-motion tensors $\mathbf{U}_p = \langle \mathbf{u}_p \mathbf{u}_p' \rangle$ relative to the same atom *p*, but also the tensors $\mathbf{U}_{pp'} = \langle \mathbf{u}_p \mathbf{u}_{p'}' \rangle$ between different atoms *p* and *p′*, the experimental bond lengths can be corrected for thermal motion in the most general case, using the procedure of Scheringer (1972) or of Johnson (1980) [see also Filippini & Gramaccioli (1989)].

The results are shown in Table 6. At room temperature, the bond-length correction for the Si—O bonds amounts to 0·003 Å, at 77 K to 0·002 Å and at 1273 K to 0·010 Å; this correction is almost the same for all these bonds. If the SiO_4 groups are essentially rigid, the corrected bond distances should essentially maintain their values at all temperatures; however, this does not seem to be the case, if Hazen's results (which represent the only set of accurately refined structures for various values of temperature and pressure) are taken as standards.

A close inspection of Hazen's data reveals some problematical features: for instance, there is a consistent difference between his Si—O(2) distance at room temperature and the corresponding values reported by all the other authors here mentioned, who find it to be appreciably larger (from 0·014 to 0·021 Å). The behaviour of the uncorrected bond distances with respect to increasing temperature is quite irregular and far from a general apparent decrease, as it should be for a rigid body [see, for instance, Schomaker & Trueblood (1968)].

Because of the presence of systematic errors in Hazen's data, these are not the best data for testing the rigidity of the SiO_4 group. Another possibility for such tests is to check the fit of the individual a.d.p.'s to a rigid body, using the experimental results obtained by other authors. In Table 7 the results from a Schomaker–Trueblood fit to this group using the room-temperature data of Bocchio *et al.* (1986) are given, and the corresponding libration corrections to the Si—O bonds are also reported.

The agreement between the observed U's of the Si and O atoms and the corresponding calculated values from the Schomaker–Trueblood fit is very good, the maximum difference barely exceeding 3σ (in one case only), and in most cases being below the standard deviation. This is evidence in favour of

Table 7. *An example of Schomaker & Trueblood's rigid-body fit to experimental U_{ij}'s in the* SiO_4 *tetrahedron of forsterite using the room-temperature data of Bocchio et al.*

T × 10^4 (Å^2)	29 (2)	0	1 (2)	Eigenvalues of **T**	50 (2)
		50 (2)	0	(× 10^4 Å^2)	42 (2)
			42 (2)		29 (2)
L × 10^4 (rad^2)	5 (2)	0	2 (2)	Eigenvalues of **L**	4·2 (4)
		9 (2)	0	(deg^2)	3·1 (6)
			12 (1)		1·5 (8)
S × 10^4 (Å rad)	0	0 (1)	0		
	1 (1)	0	−2 (1)		
	0	2 (2)	0		

Thermal libration corrections (Å)

Si—O(1) = 0·001; Si—O(2) = 0·002; Si—O(3) = 0·001

rigid-body behaviour. However, the Schomaker–Trueblood room-temperature libration corrections to the experimental Si—O bonds range from 0·001 to 0·002 Å, and substantially differ from our general-formula results (0·003 Å for each case). A possible explanation of this discrepancy comes from considering the strong prevalence of the **T** tensor contribution to all the U's (the eigenvalues of **L** range from 1·5 to 4·2 deg^2); *i.e.* there is a remarkably small libration with respect to a molecular crystal at the same temperature. This is obvious on considering that the SiO_4 group is linked to the rest of the structure through the Mg atoms by ordinary chemical bonds. In view of this small librational character, the *relative* value of the **L** tensor (which determines libration corrections) is strongly influenced by the experimental uncertainties in the U's and also by a comparable effect of the internal motion.

Therefore, the problem of defining what is really a rigid body does not always lead to a clear-cut answer, especially if conditions are not those of a molecular crystal with tightly bonded atoms within each molecule. In this case the validity of a rigid-body model depends on the accuracy which is wanted, and a value of 0·001 Å or below for bond-length measurements using room-temperature data is by no means granted by easy routine application.

We are indebted to Professor Dr G. Will of the University of Bonn and to Dr R. Langen for having provided us with useful information concerning experimental crystallographic data of samples of natural forsterite.

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Systematic Prediction of New Ferroelectric Inorganic Materials in Point Group 6

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Abstract

A total of seven new families and sixteen structurally different inorganic materials with point group 6 are shown to satisfy the criteria presented previously by the present author [*Acta Cryst.* (1988), **B44**, 585–595] for predicting ferroelectricity. In case each prediction is experimentally verified, the 183 individual entries for point group 6 listed in the Inorganic Crystal Structure Database will result in over 80 new ferroelectrics, of which about 30 are rare-earth isomorphs. The total number of 'pure' ferroelectrics discovered through late 1988, as enumerated in Landolt–Börnstein [(1989), III/28*a*], is 201. Consideration of structures containing tetrahedral ions located on trigonal axes has led to a broadening of the normal symmetric double-well potential concept for displacive ferroelectrics to include asymmetric potential minima. Spontaneous polarization reversal in such cases may result neither in equal polarization magnitudes nor in equal coercive fields for the two states. Additional categories of ferroelectric substances considered include cryptoferroelectrics and also highly conductive ferroelectrics. Analysis of the database entries in space group $P6_3$ also results in the identification of over 20 structure determinations for which the assumption of polarity is probably incorrect.

Introduction

The principal structural requirement for a polar crystal to be considered as potentially ferroelectric is the presence in the unit cell of a maximum atomic displacement of about 1 Å along the polar direction from the corresponding position in which the resulting spontaneous polarization is zero (Abrahams, 1979, 1988). In addition, the largest atomic displacement from such a position must be significantly greater than about 0·1 Å or the r.m.s. amplitude of thermal displacement of that atom. Furthermore, the thermodynamic barrier to be overcome by each atom in reaching its location corresponding to zero spontaneous polarization must be less than the equivalent of an applied d.c. field that is sufficient to reverse the polarization sense but that does not exceed the dielectric strength of the material, with an estimated phase-transition temperature that does not exceed about 2000 K.

The phase-transition temperature (T_c) in a crystal satisfying the above criteria may be estimated by Abrahams, Kurtz & Jamieson's (1968) relationship, hereafter AKJ. In this, the square of the largest displacement (Δz in Å) along the polar direction from the zero spontaneous polarization position by the metal atom forming the shortest and least ionic bonds in the structure is found to be proportional to T_c:

$$T_c = (\mathscr{K}/2k)(\Delta z)^2 \text{ K} \qquad (1)$$

where $\mathscr{K}$ is a force constant, k is Boltzmann's constant and $\mathscr{K}/2k \simeq 2{\cdot}0 \times 10^4 \text{ K Å}^{-2}$.

The given structural criteria, together with the AKJ relationship, have now been systematically applied to all entries in the Inorganic Crystal

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