

POLYHEDRAL MODELING OF THE ELASTIC PROPERTIES OF
CORUNDUM (α - Al_2O_3) AND CHRYSOBERYL (Al_2BeO_4)

Andrew Y. Au and Robert M. Hazen

No. 1965

Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20008

Abstract. Coordination polyhedra in a crystal structure are considered to be the structural units in a modified rigid-ion model. In the polyhedral model the elastic constants of coordination polyhedra are used as input parameters to calculate the single-crystal elastic constants of corundum and chrysoberyl. The average deviation of the calculated elastic constants from the measured elastic constants is within 6% for corundum and within 1% for chrysoberyl.

The corundum crystal structure is composed entirely of AlO_6 octahedra, which are also major polyhedral constituents of the chrysoberyl crystal structure. The nonelectrostatic contribution of the bulk compressibility of an ideal (regular) AlO_6 octahedron is found to be 10.5 ± 0.2 Mbar, an invariant in these two crystal structures. The polyhedral elastic constants and the associated perturbational parameters are not universal, however, as demonstrated in the two crystal structures studied.

Introduction

Knowledge of the elastic properties of mantle minerals as a function of pressure and temperature is essential in the elucidation of the chemistry and mineralogy of the Earth's mantle. Experimental determinations of the elastic constants of many mantle minerals, such as β - and γ - Mg_2SiO_4 and stishovite, have been performed, but only at room temperature and atmospheric pressure. Major obstacles to such experimental determinations include a lack of suitable samples and the difficulty of obtaining measurements at elevated pressure and temperature. In the absence of experimental data, theoretical methods can be used to provide elasticity parameters to evaluate the various mineralogical models of the Earth's mantle.

The elastic properties of crystalline solids represent asymptotic long-wavelength limits of lattice vibrations, which are static properties. The interests of solid state physicists, however, are concentrated on dynamical properties, which are the general phonon dispersion phenomena. Involved lattice dynamical models, consequently, have been developed and applied to simple crystal structures such as the NaCl-type structure. It is more appropriate, however, for Earth scientists to develop simpler lattice dynamical models that focus on the long-wavelength limit to model the elastic properties of crystalline solids of geophysical interest.

Observations of polyhedral compressibilities from many different structures reveal that the compressibility of a given type of coordination polyhedron, such as the MgO_6 octahedron, is relatively uniform among various crystal structures [Hazen and Finger, 1979]. This observation suggests that the bulk compressibility of a crystal structure might be predicted provided that the compressibilities of constituent polyhedra are known. The viability of modeling elastic properties of olivines based on coordination polyhedra has been tested by Au and D. J. Weidner (in preparation), and they have shown that elastic properties of constituent coordination polyhedra in tensor form must be known a priori in order to determine the bulk compressibility of a crystal structure. The bulk compressibility of a coordination polyhedron, which is a scalar, contains neither the directional information for a crystal structure nor the details of polyhedral linkages.

The objective of this paper is to present a more general test of the polyhedral method with a two-stage approach: (1) the estimation of the elastic stiffness tensor of a metal-oxygen octahedron in a crystal structure that is composed of only this type of metal-oxygen polyhedra, and (2) the estimation of the elastic stiffness tensor of the same type of octahedron in another crystal structure that is composed of more than one type of coordination polyhedron. The polyhedral elastic parameters of the metal-oxygen octahedron in question may then be compared. The AlO_6 octahedron in both the minerals corundum and chrysoberyl is ideal for such a test.

Method

The modeling of elastic properties is performed in the context of lattice dynamics. In phenomenological models of lattice calculations there are a variety of parameterizing schemes: rigid-ion models [e.g., Born and Huang, 1954], shell models [e.g., Cowley et al., 1963], and deformable-ion models [e.g., Jaswal and Dilly, 1977]. These parameterizations are based on physical models that work well for some specific properties of lattice vibrations. A rigid-ion model, for example, is adequate only for modeling of elastic properties, whereas a shell model or a deformable-ion model is more suitable in modeling optical properties of crystalline solids. A rigid-ion model is generally limited to two-body, central-force interactions between atoms in a crystal structure; however, there is no unique means to represent noncentral and many-body forces, both of which are critical for defining the elastic properties of crystalline solids. A polyhedral approach, in which atomic clusters are chosen to be modeling units, is a physically viable alternative because the elastic constants

Copyright 1985 by the American Geophysical Union

Paper number 5L6656
0094-8276/85/005L-6656\$03.00

TABLE 1. Modeled and Observed Elastic Constants for Corundum

C_{ij}^a	PIM ^b	SM ^c	Model A1	Model A2	Observed ^d
C_{11}	3.930	4.296	6.106	5.609	4.9760
C_{33}	4.490	5.023	5.072	4.672	5.0185
C_{44}	1.540	1.616	1.349	1.445	1.4724
C_{12}	0.710	1.548	1.489	1.551	1.6260
C_{13}	0.730	1.272	1.191	1.196	1.1718
C_{14}	0.330	-0.299	-0.224	-0.230	-0.2290
K	1.851	2.544	2.766	2.626	2.5440
μ	1.585	1.522	1.824	1.743	1.6320
$\langle\sigma\rangle^e$	1.04	0.15	0.11	0.06	

Input Parameters

C_{11} (AlO_6) Mbar	22.31	21.06
C_{12} (AlO_6) Mbar	6.23	5.41
C_{44} (AlO_6) Mbar	-1.13	-0.96
B_{Al-O} Mbar	47.13	60.24
B_{O-O} Mbar	-6.98	-12.63
B_{Al-Al} Mbar	51.19	37.26
α	1.00	0.90

^aAll elastic constants in megabars.

^bResult from Iishi [1978].

^cResult from Catlow et al. [1982].

^dData from Gieske and Barsch [1968].

$$e_{\sigma}^2 = \frac{\sum^n [(C_{ij}^{obs} - C_{ij}^{calc})/C_{ij}^{obs}]^2}{n},$$

where n is the number of independent elastic constants.

of a coordination polyhedron contain information about noncentral and many-body forces.

The polyhedral method employed in this study is a modification of an equilibrium, central-force, rigid-ion model formulated by Weidner and Simmons [1972]. The formal theory of the polyhedral approach has been given in Au [1984] and Au and Weidner (in preparation). The essence of the polyhedral approach is the incorporation of polyhedral elastic constants into a rigid-ion model. Regular metal-oxygen tetrahedra and octahedra possess cubic symmetry, and their elastic properties can be represented by three constants, C_{11} , C_{12} , and C_{44} . In the polyhedral method the three elastic constants of a polyhedron are inverted by finite element analysis into interatomic coupling coefficients between near-neighbor atoms within the polyhedron.

In this study a Coulombic calculation is performed to determine the long-range, two-body, central-force coupling coefficients in a unit cell. The observed structure of the crystal and full ionic charges of a unit cell are used in these electrostatic calculations. Structural data on corundum at room temperature and atmospheric pressure are taken from Ishizawa et al. [1980], and those on chrysoberyl are taken from Hazen and Au (in preparation). In the model

calculations an ionicity parameter α , which ranges from 0 to 1, is used as a free parameter. This parameter uniformly scales the ionic charges of the ions in a unit cell and hence defines the covalency of the crystal structure in this model.

Two types of short-range force are considered in this model. The first is a set of near-neighbor, two-body, central forces that are used to balance the Coulombic forces so that the crystal structure retains equilibrium. These short-range forces can be either attractive or repulsive, and they are a function of the assigned ionicity of the crystal structure. The second type of short-range force is given by a set of interatomic coupling coefficients that are related to the strength of a bond between near-neighbor ions.

If a crystal structure is composed of regular coordination polyhedra, a complete set of short-range interatomic coupling coefficients can be obtained merely from the input elastic constants of the constituent polyhedra. A breakdown of the Cauchy relation in the elastic constants (i.e., if C_{12} and C_{44} are not equal) indicates the presence of noncentral and many-body forces. These polyhedral elastic constants are free parameters in this study. Coordination polyhedra in typical minerals, however, are distorted, and perturbations are necessary to account for these polyhedral distortions. In this study the interatomic coupling coefficients are perturbed as a linear function of the deviation from an assumed equilibrium bond distance. The perturbational spring coefficient is given as

$$k(r) = B(r - a), \quad (1)$$

where k is the anharmonic coupling coefficient; r is the corresponding interatomic distance; a is an assumed equilibrium distance; and B, a free parameter, is an anharmonic spring coefficient.

In this model the values of all free parameters are optimized to search for a best fit to the measured single-crystal elastic constants. A measure of the agreement between the calculated and measured values is expressed in terms of a goodness-of-fit parameter $\langle\sigma\rangle$, which is the standard deviation of the calculated values from the observed values.

Results and Discussion

The calculated strength of electrostatic interactions in a crystal structure is dependent upon the value of the ionicity parameter α , which is found to be the most sensitive parameter in this static lattice calculation. The magnitude and nature of a set of short-range equilibrium forces are, therefore, strong functions of the assigned ionicity.

Corundum

Seven free parameters are used in the corundum model calculations: an ionicity parameter, three elastic constants that represent the elastic properties of a regular AlO_6 octahedron, and three anharmonic spring coefficients. Two of the three anharmonic spring coefficients are related to the intrapolyhedral Al-O and O-O bonds. The third coefficient is related to the interpoly-

TABLE 2. Modeled and Observed Elastic Constants for Chrysoberyl

C_{ij}^a	Model C1	Model C2	Observed ^b
C_{11}	5.066	5.277	5.2770
C_{22}	4.400	4.382	4.3870
C_{33}	4.402	4.653	4.6580
C_{44}	1.464	1.437	1.4440
C_{55}	1.410	1.457	1.4580
C_{66}	1.518	1.520	1.5180
C_{12}	1.264	1.251	1.2500
C_{13}	1.301	1.280	1.2800
C_{23}	1.097	1.112	1.1100
K	2.347	2.390	2.3910
μ	1.553	1.585	1.5880
$\langle\sigma\rangle$	0.03	0.002	

Input Parameters

C_{11} (AlO_6) Mbar	40.01	26.48
C_{12} (AlO_6) Mbar	0.04	2.27
C_{44} (AlO_6) Mbar	-3.47	0.22
C_{11} (BeO_4) Mbar	31.16	14.88
C_{12} (BeO_4) Mbar	-21.09	0.97
C_{44} (BeO_4) Mbar	20.39	42.09
B_{Al-O} Mbar	143.25	127.93
B_{O-O} Mbar	20.25	8.86
B_{Al-Al} Mbar	-82.04	-23.86
B_{Be-O} Mbar	1072.95	230.19
α	1.00	0.652

^aAll elastic constants in megabars.

^bData from Wang and Gupta [1975].

hedral face-sharing and edge-sharing Al-Al interactions. The Al-O, O-O, and Al-Al distances are assumed to be 1.912, 2.719, and 2.723 Å, respectively, which are the averages of the corresponding observed [Ishizawa et al., 1980] interatomic separations in corundum.

The model calculations for corundum are performed in two stages (Table 1), model A1 and model A2. Full ionic charges are assumed on all the ions in a corundum unit cell in model A1 (i.e., the ionicity parameter α is set to 1). Other free parameters are optimized to obtain the best fit with measured values of the independent elastic constants. The goodness of fit in this model calculation is $\langle\sigma\rangle = 0.11$. This result means that the average deviation of the calculated from the observed elastic constants is within 11% (see Table 1). The agreement between the calculated and observed C_{11} is relatively poor, the calculated C_{11} being 23% larger than the observed value.

In model A2 the ionicity parameter is also optimized along with the other six free parameters. The best agreement with the observed elastic constants is found to occur at approximately $\alpha = 0.9$. Agreement between the calculated and the measured C_{11} in model A2 is significantly improved; the calculated value is 13% larger than the observed value (Table 1). The goodness of fit $\langle\sigma\rangle$, accordingly, is improved to 0.06. The overestimation of C_{11} may suggest

that Al-Al repulsions across the octahedral shared edges are more shielded than indicated by a rigid-ion model. The actual source of this discrepancy is, however, unknown, and it cannot be resolved in the context of the present model. The goodness of fit in this model can be improved by the assignment of individual free parameters to the eight crystallographically distinct, near-neighbor Al-O, O-O, and Al-Al bonds in the corundum structure. Such additional parameterizations, however, are not warranted because they make no additional contribution to the understanding of the nature of interatomic forces.

Recent lattice dynamical calculations of corundum include those of Iishi [1978] and Catlow et al. [1982]. Interatomic coupling coefficients vary as a function of frequency, as demonstrated by Keating [1966]. The same set of coupling coefficients in an ionic model cannot satisfy the phenomena of lattice vibrations in the two asymptotic limits of static and dynamical properties. A polarizable-ion model applied by Iishi [1978] reproduces the observed optical frequencies well, but not the elastic properties (Table 1). Catlow et al. [1982] have used a simple shell model in which frequency-dependent, shell-core, coupling springs are parameterized. The simple shell model, however, is also limited; it reproduces the optical properties well, but not the elastic properties (Table 1). The polyhedral model represents a significant improvement over previous work in modeling elastic properties.

The long-range forces in this static lattice calculation are accounted for by Coulombic interactions. The polyhedral elastic constants of a regular polyhedron and the perturbational coefficients reflect only the short-range interatomic coupling forces between the intrapolyhedral ions. The optimized elastic constants of a regular AlO_6 octahedron as well as the perturbational parameters, however, are not constant as a function of ionicity (i.e., the seven free parameters are not independent). The AlO_6 octahedron in the corundum structure is distorted, and therefore the polyhedral elastic properties should be represented not only by the three elastic constants of a regular octahedron, but also by the polyhedral perturbational parameters.

The nonelectrostatic contribution of the bulk compressibility of a regular AlO_6 octahedron is estimated from the optimized polyhedral elastic constants in model A2 to be 10.6 Mbar. The bulk compressibility K is given as

$$K = (C_{11} + 2C_{12})/3, \quad (2)$$

where C_{11} and C_{12} are the polyhedral elastic constants.

Chrysoberyl

Chrysoberyl, Al_2BeO_4 , is of interest because it is isomorphous with the geophysically relevant mineral olivine. There are eleven free parameters in the chrysoberyl model calculations: an ionicity parameter, three elastic constants that represent the elastic properties of a regular AlO_6 octahedron, three elastic constants that represent the elastic properties of a regular BeO_4 tetrahedron, and four anharmonic spring coef-

ficients of the near-neighbor Al-O, O-O, Al-Al, and Be-O bonds. The equilibrium Al-O, O-O, and Al-Al distances are the same as in the corundum model calculations. The equilibrium Be-O distance is assumed to be the average of the observed Be-O interatomic separations in bromellite (BeO in wurtzite structure), which is 1.647 Å.

The chrysoberyl model calculations are performed in two stages (Table 2). In model C1 the ionicity parameter α is set to 1. The Be-O anharmonic coefficient in this model calculation is an order of magnitude larger than the other anharmonic coefficients. This large anharmonic correction made the Be-O coupling coefficient very large and hence implies a very stiff Be-O bond. The observation of a very stiff Be-O bond in the calculation is borne out in a recent high-pressure, single-crystal, structure refinement of chrysoberyl (Hazen and Au, in preparation). For chrysoberyl the agreement between calculated and observed values is much closer than for corundum. The goodness-of-fit parameter $\langle\sigma\rangle$ is 0.03 in model C1. In model C2 the ionicity parameter is optimized and is found to be approximately $\alpha = 0.65$. Agreement between calculated and observed elastic constants is significantly improved (Table 2): the goodness-of-fit parameter $\langle\sigma\rangle$ is 0.002. The nonelectrostatic contribution of the bulk compressibility of the regular AlO_6 octahedron estimated from model C2 is 10.3 Mbar, compared with 10.6 Mbar estimated from model A2 for corundum. The nonelectrostatic contribution of the bulk compressibility of a polyhedron, approximately 10.5 Mbar as it is inferred in this study, may thus represent an invariant polyhedral property. Further studies on aluminum-bearing oxides and silicates are required to test this possibility.

Concluding Remarks

The electrostatic contribution of the polyhedral bulk compressibility depends on the structure and ionic environment of the host crystal. The individual polyhedral parameters may vary from one structure to another. Ionic environment, as well as the polyhedral linkage and distortions of the AlO_6 octahedra in the corundum and chrysoberyl structures, is different. Different sets of perturbational parameters are thus necessary to account for the elastic properties of a distorted polyhedron in general tensor form.

The significant improvement, compared with previous lattice dynamical models, between calculated and measured elastic constants of corundum and chrysoberyl supports polyhedral modeling as a viable approach to study the elastic properties of crystalline solids. This approach provides an alternative mechanism to represent noncentral and many-body forces in crystal structures of geophysical interest. The various schemes of polyhedral linkage and distortion in crystal structures provide a means to model the polyhedral parameters as a function of polyhedral distortions. Further polyhedral modeling on isostructural and isochemical series and study of their systematic trends are needed

to deduce an invariant set of polyhedral parameters. A study of polyhedral systematics should contribute to the prediction of elastic constants of mantle minerals as a function of pressure and temperature.

Acknowledgments. The authors would like to thank Drs. J. W. Downs, A. M. Hofmeister, K. A. Goettel, G. E. Muncill, M. W. Schaefer, and H. S. Yoder, Jr., for thoughtful discussions and critical review of the manuscript. This research is supported by National Science Foundation grant EAR83-19209.

References

- Au, A. Y., Theoretical modeling of the elastic properties of mantle silicates, Ph.D. thesis, 134 pp., SUNY, Stony Brook, 1984.
- Born, M., and K. Huang, Dynamical Theory of Crystal Lattices, 420 pp., Clarendon Press, London, 1954.
- Catlow, C. R. A., R. James, W. C. Mackrodt, and R. F. Stewart, Defect energetics in $\alpha-Al_2O_3$ and rutile TiO_2 , Phys. Rev. B, **25**, 1006-1026, 1982.
- Cowley, R. A., W. Cochran, B. N. Brockhouse, and A. D. B. Woods, Lattice dynamics of alkali halide crystals. III. Theoretical, Phys. Rev., **131**, 1030-1039, 1963.
- Gieske, J. H., and G. R. Barsch, Pressure dependence of the elastic constants of single crystalline aluminum oxide, Phys. Status Solidi, **29**, 121-131, 1968.
- Hazen, R. M., and L. W. Finger, Bulk modulus-volume relationship for cation-anion polyhedra, J. Geophys. Res., **84**, 6723-6728, 1979.
- Iishi, K., Lattice dynamics of corundum, Phys. Chem. Miner., **3**, 1-10, 1978.
- Ishizawa, N., T. Miyata, I. Minato, F. Marumo, and S. Iwai, A structural investigation of $\alpha-Al_2O_3$ at 2170K, Acta Crystallogr., Sect. B, **36**, 228-230, 1980.
- Jaswal, S. S., and V. D. Dilly, Deformable-ion model and lattice dynamics of LiD , Phys. Rev. B, **15**, 2366-2370, 1977.
- Keating, P. N., Effect of invariance requirements on the elastic strain energy of crystals with application to the diamond structure, Phys. Rev., **145**, 637-645, 1966.
- Wang, H., and M. C. Gupta, Chrysoberyl (Al_2BeO_4): anomaly in velocity-density systematics, J. Geophys. Res., **80**, 3761-3764, 1975.
- Weidner, D. J., and G. Simmons, Elastic properties of alpha quartz and the alkali halides based on an interatomic force model, J. Geophys. Res., **77**, 826-847, 1972.

A. Y. Au and R. M. Hazen, Geophysical Laboratory, Carnegie Institution of Washington, 2801 Upton St., N. W., Washington, DC 20008.

(Received July 29, 1985;
accepted August 15, 1985.)