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Elasticity of diopside $CaMgSi_2O_6$ measured by means of the resonant sphere technique, RST

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Resonant frequencies for a single crystal diopside sphere are measured accurately and thirteen elastic moduli are reduced by the least squares calculation. A set of moduli gives theoretical resonant frequencies close enough to the observed ones.

keyword: diopside, single crystal, resonace, sphere, elasticity

I. Introduction

Diopside ($CaMgSi_2O_6$) is considered to be much abundant in the Earth's mantle, below the Moho boundary, rather than in the crust, the outermost shell. In the Earth's upper mantle, diopside is the second abundant mineral as well as garnet, orthopyroxene and spinel, while olivine is the dominant component. Diopside belongs to monoclinic crystal system, and therefore, it has thirteen non-zero independent elastic moduli. Such a number of elastic moduli are difficult to be determined by the pulse transmission methods, because many ray paths are required to determine them. Resonance methods are convenient to this difficulty in number of specimens. One specimen is enough to determine the thirteen elastic moduli, if quality and size of the specimen are adequate for resonance measurement.

After success of the sphere resonance method to determine six elastic moduli of a mineral rutile with tetragonal crystal symmetry [Suzuki et al, 1992a], nine elastic moduli and their quality factors were determined for a small natural olivine specimen [Suzuki et al. 1992b]. After those we tried to determine elastic moduli for a sphere specimen of diopside. But, we unfortunately failed to identify the oscillatory modes, because of much difference between observed and calculated frequencies. Recently, Isaak and Ohno [2003] and Ohno [2003] succeeded to determine thirteen elastic moduli of diopside by the resonance method with a rectangular parallelepiped specimen. We again tried to calculated using their results as initial values for the least squares calculation. Through this process,

Table 1. Specimen

Composition	$CaMgSi_2O_6$
Crystal system	monoclinic
Independent elastic moduli	13
Average diameter	2.1355 (8) mm
Density	3,287 (8) kg/m^3

Numeral in parentheses shows probable error in the last place of the average value.

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we could show that observed and calculated frequencies agree fairly well, and finally we could obtain thirteen elastic moduli of the diopside specimen.

The names of resonance methods historically include the shape of a specimen such as "sphere", because an important part of the method is how to evaluate eigenfrequency accurately and it was possible for a specific shape of a specimen. Visscher et al.[1991] systematically described to include some shapes. Recently, resonance methods to determine physical properties of solids is called the resonant ultrasound spectroscopy RUS, irrespective of the shape of specimens, in other laboratories.

II. Measurement and calculation

The specimen we used for resonance measurement was grown artificially (by M.M.) and has the end member composition. Basic parameters are shown in Table 1. Thirteen moduli to be determined are shown in Figure 1, and the orthogonal coordinates defining them are shown in Figure 2. We measured forty one resonance modes between 1.5 and 3.5 MHz (Table 2). Lower half of the measured resonance frequencies are shown in Figure 3, and compared with calculated frequency with elastic moduli from other sources.

For determination of elastic moduli, it is necessary to compute eigenfrequencies accurate enough as compared with the observed resonance frequencies f^o. The theoretical frequencies f^c are calculated with the *xyz* algorithm [Visscher et al, 1991], in which the basis functions are the power of the orthogonal coordinates $x^l y^m z^n$ and we used the sum of the power $N = l+m+n = 11$.

The residual equation for the least squares calculation to obtain elastic moduli from observed frequencies is written as

$$f_k^o - f_k^c = \Delta f_k = \sum_{i,j} \frac{\partial f_k}{\partial C_{ij}} \Delta C_{ij} + \delta_k \quad ; \quad i \le j \le 6 \qquad \text{.... (1)}$$

$$\Delta C_{ij} = C_{ij}^s - C_{ij}^r$$

where k represents forty one observed and calcu-

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & \circ & \circ & C_{16} \\ * & C_{22} & C_{23} & \circ & \circ & C_{26} \\ * & * & C_{33} & \circ & \circ & C_{36} \\ \circ & \circ & \circ & C_{44} & C_{45} & \circ \\ \circ & \circ & \circ & * & C_{55} & \circ \\ * & * & * & \circ & \circ & C_{66} \end{pmatrix}$$

Figure 1. Matrix of thirteen independent elastic moduli of monoclinic symmetry shown as a 6x6 matrix by the Voigt notation C_{ij}. * : same value to the upper right component at the symmetric cite, $C_{ij}=C_{ji}$. o : zero value.

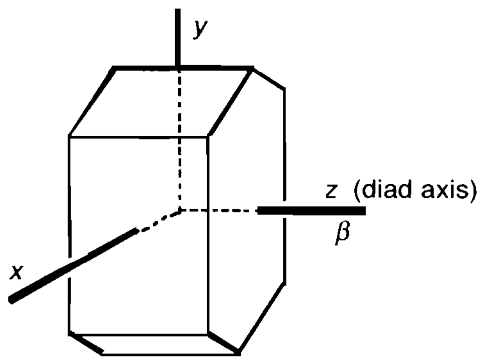

Figure 2. The orthogonal *x*, *y* and *z* axes of diopside corresponding to definition of moduli in Figure 1.

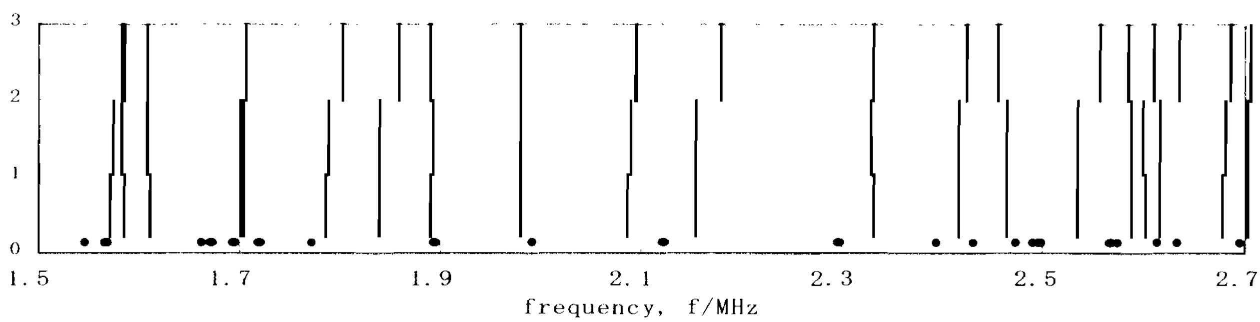

Figure 3. Comparison of resonant spectrum. top: calculated f^c with C_{ij} by Ohno, 2003; middle: regressive calculation by the least squares method for f^o; bottom: observed f^o; solid circle: f^c from C_{ij} by Levien et al., 1979.

lated frequencies, ΔC_{ij} is thirteen unknowns, which are differences of elastic moduli of the specimen C_{ij}' to be determined and C_{ij}^r is initial values of moduli for theoretical calculation of frequencies. Since the relation between eigen frequency and elastic moduli is nonlinear, iterative calculation was applied for ΔC_{ij} till convergence. The normal equation derived from Eq.(1) is ,

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1,13} \\ : & a_{22} & a_{23} & \cdots & a_{2,13} \\ : & : & a_{33} & \cdots & a_{3,13} \\ : & : & : & : & : \\ a_{1,13} & a_{2,13} & a_{3,13} & \cdots & a_{13,13} \end{pmatrix} \begin{pmatrix} \Delta C_1 \\ \Delta C_2 \\ \Delta C_3 \\ : \\ \Delta C_{13} \end{pmatrix} = \begin{pmatrix} m_1 \\ m_2 \\ m_3 \\ : \\ m_{13} \end{pmatrix}. \quad (2)$$

where ΔC_i is thirteen unknowns to be determined. Actually the determinant of this matrix is too small to be of the order of 10^{-12}, so we tried to solve the equation by a method giving a small perturbation ε to the diagonal components, i.e., $a_{ii} \times (1+\varepsilon)$ (i =1, 2, . . . 13). The value of ε given here are from 10^{-3} to 10^{-5} [Saito, 1983]. Through iterative calculation of the least squared method, we could reduce the root mean squares to be rms=0.93 kHz, or relatively 0.05%. Using the elastic moduli thus determined, we calculated resonant frequencies f, which are close enough to observed frequencies f^o as shown in middle line in Figure 3. Dots show calculated frequencies with the previous moduli [Levien, et al, 1979], which are difficult to correlate with observed frequencies f^o. All the f^o and f^c are compared in Table 2

On the other hand, when we gave small values of ε less than 10^{-6}, we could not obtain solutions or had too large value of rms.

III. Results

After trials, we obtained a set of moduli shown in the row (d) in Table 3, where some of previous reports are listed for comparison. Isotropic moduli are obtained by the Voigy-Reuss-Hill averaging scheme and then elastic wave velocities, too. The results are as follows:

bulk modulus K_S = 113.62 GPa
rigidity modulus G = 72.15 GPa
compressional wave velocity V_p = 7.99 km/s
shear wave velocity V_s = 4.68 km/s

where density is ρ =3,287 (8) kg/m^3 .

These results of velocity are plotted in Figure 4, together with those of mantle candidate minerals previously reported from our and colleague's laboratories [Aizawa et al., 2003, Mayama et al., 2003, Oda et al., 1992, Suzuki et al., 2000, Suzuki et al., 2000 ~ 2002] . It can be seen that elastic wave velocities of diopside are close to those of calcium oxide CaO. In the deeper Earth's mantle, calcium ions exist in high pressure phases of Ca-garnet and CaSiO3-perovskite. Calcium ion may lower density and velocities

Table 2. Observed and calculated frequencies of the diopside sphere.
Relative difference $r = 100 \times \Delta f / f^c$

No.	f^o/MHz	f^c/MHz	Δf/MHz	r / %
1	1.57262	1.57348	-0.00086	-0.054
2	1.58317	1.58210	0.00107	0.068
3	1.61055	1.60972	0.00083	0.052
4	1.69894	1.69887	0.00007	0.004
5	1.70149	1.70148	0.00001	0.001
6	1.78515	1.78523	-0.00008	-0.004
7	1.83815	1.83779	0.00036	0.020
8	1.89110	1.89140	-0.00030	-0.016
9	1.97833	1.97804	0.00029	0.015
10	2.08594	2.08664	-0.00070	-0.033
11	2.15435	2.15460	-0.00025	-0.012
12	2.32925	2.32823	0.00102	0.044
13	2.41660	2.41671	-0.00011	-0.004
14	2.46286	2.46361	-0.00075	-0.030
15	2.53264	2.53352	-0.00088	-0.035
16	2.58588	2.58593	-0.00005	-0.002
17	2.60073	2.59870	0.00203	0.078
18	2.61396	2.61466	-0.00070	-0.027
19	2.67668	2.67907	-0.00239	-0.089
20	2.70248	2.70256	-0.00008	-0.003
21	2.72469	2.72496	-0.00027	-0.010
22	2.73803	2.74004	-0.00201	-0.073
23	2.74700	2.74500	0.00200	0.073
24	2.86049	2.86222	-0.00173	-0.060
25	2.86773	2.86675	0.00098	0.034
26	2.90646	2.90612	0.00034	0.012
27	2.95268	2.95205	0.00063	0.021
28	2.97339	2.97325	0.00014	0.005
29	3.14367	3.14492	-0.00125	-0.040
30	3.22178	3.22136	0.00042	0.013
31	3.26540	3.26433	0.00107	0.033
32	3.27477	3.27593	-0.00116	-0.035
33	3.28609	3.28600	0.00009	0.003
34	3.29458	3.29537	-0.00079	-0.024
35	3.33015	3.32915	0.00100	0.030
36	3.36436	3.36372	0.00065	0.019
37	3.37107	3.37071	0.00036	0.011
38	3.39853	3.39816	0.00037	0.011
39	3.41851	3.41824	0.00027	0.008
40	3.45956	3.45933	0.00023	0.007
41	3.51410	3.51348	0.00062	0.018

rms/MHz= 0.00093

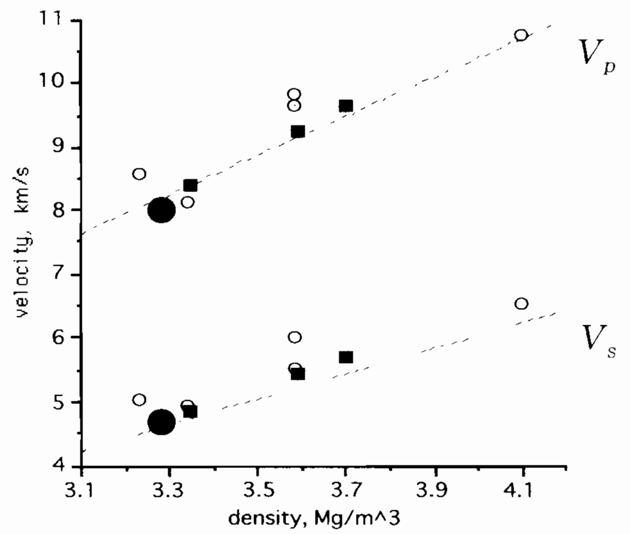

Figure 4. Compressional and shear wave velocities (*Vp* and *Vs*, km/s) of diopside are plotted against density Mg/m^3=g/cm^3 on the Birch diagram. Heavy dot: diopside; Open circle: iron free minerals; Square: from left to right, alpha, beta and gamma phases with composition of $(Mg_{0.91} Fe_{0.09})_2 SiO_4$. Dotted line: empirical velocity-density relationship with the mean atomic weight m = 21.

Table 3. Comparison of elastic moduli of diopsides. unit in Mbar = 100 GPa. The parentheses at the column (d) represent errors at the last digits.

C_{ij}	(a)	(b)	(c)	(d)	
C_{11}	2.23	2.378	2.244	2.306	(10)
C_{22}	2.35	2.295	2.396	2.366	(43)
C_{33}	1.71	1.836	1.817	1.777	(2)
C_{23}	0.57	0.599	0.615	0.579	(4)
C_{31}	0.77	0.835	0.783	0.787	(4)
C_{12}	0.81	0.800	0.686	0.711	(17)
C_{44}	0.74	0.765	0.799	0.780	(4)
C_{55}	0.66	0.816	0.786	0.788	(4)
C_{66}	0.67	0.730	0.704	0.696	(16)
C_{45}	0.073	0.084	0.068	0.077	(1)
C_{16}	0.17	0.090	0.096	0.102	(5)
C_{26}	0.43	0.481	0.463	0.455	(6)
C_{36}	0.07	0.095	0.079	0.079	(5)
K_s	1.129	1.172	1.143	1.136	
G	0.671	0.723	0.726	0.721	

(a) Levien, et al, 1979; (b) Collins & Brown, 1998; (c) Ohno, 2003; (d) this study. Source of specimens:(a) and (b), natural; (c) and (d) synthesized end member.

of these phases. Elastic data of these Ca-containing phases are needed to clarify structure, composition and dynamics of the Earth's interior, in detail.

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