

Temperature dependence of elastic moduli of β - and γ -(Mg,Fe)₂SiO₄: Supplements

Norihito MAYAMA* and Isao SUZUKI*

We measured the resonant frequencies for sphere specimens of the high pressure phases, β - and γ -(Mg_{0.91}Fe_{0.09})₂SiO₄ from 298 to 470 K. The adiabatic bulk modulus K_S and shear modulus μ at 298 K were determined to be $K_S=165.72(6)$, $\mu=105.43(2)$ GPa for the β -phase, and $K_S=185.1(2)$, $\mu=118.22(6)$ GPa for the γ -phase, respectively. The average slopes of the moduli at the measured temperature ranges were found to be $\partial K_S/\partial T=-0.0175(3)$, $\partial\mu/\partial T=-0.0159(1)$ GPaK⁻¹ for the β -phase and $\partial K_S/\partial T=-0.0193(6)$, $\partial\mu/\partial T=-0.0148(3)$ GPaK⁻¹ for the γ -phase. The numerals in parentheses indicate probable errors in the last place. In this technical report, we describe the observed frequencies and calculation method to obtain elastic moduli, in details.

Keywords: Wadsleyite, Ringwoodite, Elastic moduli

1. Introduction

Wadsleyite (β -phase) and ringwoodite (γ -phase) are high-pressure polymorphs of olivine and supposed to be major constituents of the upper mantle. Therefore the elastic properties for the β - and γ -phases have been measured in many studies [e.g., Sawamoto *et al.*, 1984; Weidner *et al.*, 1984]. Recently, we reported in short papers [Mayama *et al.*, 2004a; b]. The purposes of this report are to put the following materials used in data reduction on record: observed resonant frequencies and reduced elastic moduli against temperature, extrapolation of elastic moduli to higher temperatures, and related materials.

2. Specimen and Measurement

The specimens were synthesized and sintered from San Carlos olivine using a Kawai-type high-pressure apparatus (USSA5000 in the Institute for Study of the Earth's Interior). The conditions on high pressure syntheses are listed in Table 1. The polycrystalline specimens were confirmed to be uniform under microscope and good in crystallinity from the narrow widths of x-ray diffraction peaks. The electron microprobe analyses were made for the specimens and the Fe/(Mg+Fe) ratio was found to be 0.09, which was the same as that of starting material. Density and diameters of the sphere specimens are summarized in Table 2. Values of density at room temperature are in good agreement with X-ray densities [Sinogeikin *et al.*, 1998], suggesting that our specimens are almost pore-free.

The resonant spectra of the specimens at room temperature were measured by the common frequency scanning method, or the CW method [Suzuki *et al.*, 1992]. The frequency range of measurement was from 1.8 to 5.0

MHz with 10 Hz intervals. The resonant frequency shifts caused by supporting force for the specimens were corrected by using the contacting sphere theory [Yoneda, 2002].

High temperature measurements were made with the buffer rod method to protect transducers [Goto and Anderson, 1988]. To save time in data acquisition, another method called the FT method [Suzuki *et al.*, 1994] was applied. The damping waveform of the specimens stimulated by high voltage pulses were stacked and averaged up over five thousand times to reduce random noises from circumstances. The sampling rate is 5 MHz and data length is 5 ms. Overall view and its enlargement of waveform are shown in Figure1-A, B. The resonant spectrum was obtained by the FFT analysis, in which frequency resolution was 200 Hz. The temperature range was from 298 to 470 K, and measurements were made almost at every 10 or 20 K. Temperature fluctuation during measurements was within 1 K. The diameter and density of the specimens at high temperature were corrected by thermal expansion data of Suzuki *et al.* [1979; 1980] and shown in Table 2. The

Table 1. Conditions for syntheses and composition of yielded samples.

	β -phase	γ -phase
P /GPa	14	18
T /K	1400	1200
t /hr	1	2
composition	(Mg _{0.91} Fe _{0.09}) ₂ SiO ₄	(Mg _{0.91} Fe _{0.09}) ₂ SiO ₄
t :duration time		

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Table 2. Diameter and density versus temperature of the β - and γ -phase specimens used for data reduction.

T/K	β -phase		γ -phase	
	d/mm	ρ/Mgm^{-3}	d/mm	ρ/Mgm^{-3}
298	2.250(2)	3.60(1)	1.830(2)	3.70(1)
300	2.2501	3.6023	1.8303	3.7015
310	2.2502	3.6015	1.8304	3.7008
320	2.2504	3.6007	1.8305	3.7001
330	2.2506	3.5999	1.8307	3.6994
340	2.2508	3.5991	1.8308	3.6986
350	2.2509	3.5983	1.8309	3.6978
360	2.2511	3.5974	1.8310	3.6971
370	2.2513	3.5965	1.8312	3.6963
380	2.2515	3.5956	1.8313	3.6955
390	2.2517	3.5947	1.8314	3.6947
400	2.2519	3.5938	1.8316	3.6938
410	2.2521	3.5929	1.8317	3.6930
420	2.2522	3.5920	1.8318	3.6922
430	2.2524	3.5910	1.8320	3.6913
440	2.2526	3.5900	1.8321	3.6905
450	2.2528	3.5891	1.8323	3.6896
460	2.2531	3.5881	1.8324	3.6887
470	2.2533	3.5871	1.8325	3.6879

d: diameter, ρ : density, $\text{Mg/m}^3 = \text{g/cm}^3$

Table 3. Resonant frequencies of the β - and γ -phase specimens at room temperature.

mode	β -phase	γ -phase
	f/kHz	f/kHz
${}_0T_2$	1913.89	2457.00
${}_0S_2$	2019.98	2595.15
${}_1S_1$	2600.33	3337.14
${}_0T_3$	2957.41	3796.11
${}_0S_3$	2994.06	3847.11
${}_0S_0$	3309.89	4243.44
${}_1S_2$	3695.18	4739.32
${}_0S_4$	3828.21	n.d.
${}_0T_4$	3897.94	5003.00
${}_1T_1$	4413.37	n.d.
${}_0S_5$	4608.31	n.d.
${}_0T_5$	4792.05	n.d.
${}_1S_3$	4905.65	n.d.

n.d. : no data

resonant frequencies obtained at high temperatures under supporting force were reduced by the correction terms at the ambient condition [Yoneda, 2002]. The elastic

moduli (adiabatic bulk (K_S) and shear (μ) moduli) at every temperature were calculated from the resonant frequencies by the least squares method

$$f_k^o - f_k^c = \left(\frac{\partial f_k^c}{\partial K_S}\right)\Delta K_S + \left(\frac{\partial f_k^c}{\partial \mu}\right)\Delta\mu + \delta_k \quad (1)$$

($k=1,2,\dots$)

where f^o and f^c are observed and calculated frequency, $\Delta K_S = K_S - K_S^r$, and $\Delta\mu = \mu - \mu^r$ are unknowns to be determined, K_S and μ are elastic moduli of the specimen, and K_S^r and μ^r are reference values for iterative calculation.

3. Result

In the spectrum data at room temperature, we found the 13 and 8 resonant modes for the β - and γ -phases (Table 3). The modes were well assigned with isotropic oscillation. The half-widths of resonant peaks were about 1 kHz. Examples of damping waveforms at high temperature are shown in Figure 1. After the FFT analysis, the lower 9 and 6 modes for the β - and γ -phases were found even from the data obtained through buffer rods, and the higher frequency modes were not detected because of their smaller amplitudes. We had a sufficient number of modes for reduction of the isotropic elastic moduli. Temperature dependence of resonant frequencies for the β - and γ -phases are shown in Table 4. The differences of resonant frequencies between heating and cooling processes are very small to be 0.05 % maximum. The elastic moduli at every temperature were calculated from the resonant frequencies by the least squares method. Temperature dependence of elastic moduli for the β - and γ -phases are shown in Table 5 and Figure 2.

In order to estimate elastic moduli at high temperatures we used the modified-Wachtman's equation, [Anderson, 1966; Suzuki et al., 2000]

$$M(T) = M_0 - gE(\theta, T) \quad (2)$$

where $M(T)$ is an elastic modulus as a function of temperature T , and the $E(\theta, T)$ is thermal energy evaluated by the Debye model. Both of $E(\theta, T)$ and $M(T)$ are almost linear against temperature for $T > 1.3 \times \theta$. The M_0 , g and θ are constants to be determined by the curve fitting to $M(T)$ data. The equation (2) was applied for curve fitting to the present data and we obtained three constants. In the constants, the Debye temperature was somewhat larger than the acoustic ones, and so we applied Eq. 2 giving the well determined acoustic Debye temperatures, $\theta_{ac}=841$ and 884 K for the β - and γ -phases, respectively. They are evaluated by

$$\theta_{ac} = \left(\frac{\hbar}{k}\right) \left(\frac{4\pi m}{9\rho}\right)^{\frac{1}{3}} \left(\frac{1}{v_p^3} + \frac{2}{v_s^3}\right)^{\frac{1}{3}} \quad (3)$$

Here the \hbar and k are Planck's and Boltzmann's constants.

Table 4. Temperature changes of observed resonant frequencies of the β - and γ -phase specimens.

β -phase								
T/K	${}_0T_2$	${}_0S_2$	${}_1S_1$	${}_0T_3$	${}_0S_3$	${}_0S_0$	${}_1S_2$	${}_0T_4$
heating								
297	1913.9	2020.0	2600.3	2957.4	2994.1	3309.9	3695.2	3897.9
300	1913.7	2019.8	2600.1	2957.0	2993.9	3309.7	3694.4	3897.5
310	1912.7	2018.6	2598.5	2955.2	2989.9	3308.1	3692.2	3895.1
320	1911.7	2016.3	2596.9	2952.6	n.d.	3306.3	3690.2	3892.7
330	1910.3	2015.3	2595.1	2951.2	2986.5	3304.7	3687.8	3890.1
340	1909.1	2014.0	2593.5	2949.4	2985.7	3303.3	3685.6	3886.7
350	1906.9	2011.6	n.d.	2946.6	2983.5	3301.5	3683.4	3884.7
360	1905.3	2010.0	2589.3	2944.2	2981.9	3300.1	3680.4	3881.7
370	1904.3	2009.2	2588.3	2942.6	2981.1	3298.1	3678.6	3879.5
380	1902.9	2008.0	2587.1	2940.6	2977.3	3296.5	3676.6	3877.3
390	1901.7	2006.6	2585.3	2937.4	2975.9	3294.9	3674.2	3873.5
400	1900.3	2005.2	2583.7	2935.4	2973.3	3293.3	n.d.	3871.5
410	1898.7	2003.6	2582.1	2933.2	2971.1	3291.7	n.d.	3869.3
420	1897.5	2002.2	2579.5	2931.2	2969.1	3289.3	n.d.	3864.5
430	1895.9	2000.4	2578.3	2929.0	2966.5	3287.5	n.d.	3861.9
440	1894.3	1998.6	n.d.	2926.6	2963.7	3285.7	n.d.	3858.9
450	1892.7	1997.0	n.d.	2924.6	2961.5	3284.1	n.d.	3856.3
460	1891.3	1995.6	n.d.	2922.8	2959.5	3282.5	n.d.	3853.7
470	1890.1	1994.2	n.d.	2920.4	2957.5	3280.7	n.d.	3851.7
cooling from 470 K								
300	1914.7	2019.0	2600.5	2957.6	2993.7	3310.1	3695.2	3898.3
310	1912.5	2017.4	2597.9	2955.0	2990.3	3307.5	3691.6	3894.7
330	1910.5	2014.2	2595.3	2951.4	2987.5	3304.9	3687.8	3890.1
350	1907.3	2011.8	n.d.	2946.8	2982.9	3301.5	3683.0	3884.9
370	1904.7	2009.0	2588.5	2942.8	2980.7	3298.3	3678.6	3879.9
390	1902.1	2006.4	2585.5	2937.0	2975.3	3295.1	3674.2	3873.7
410	1899.3	2003.8	2582.3	2933.4	2971.1	3291.7	n.d.	3869.7
430	1896.3	2001.0	2578.5	2929.2	2967.1	3287.7	n.d.	3862.3
450	1893.1	1997.2	n.d.	2924.8	2961.5	3284.3	n.d.	3856.3
470	1890.1	1994.2	n.d.	2920.4	2957.5	3280.7	n.d.	3851.7

n.d. : no data

The mode ${}_0S_4$ is not detected in this measurement.

The m and ρ represent mean atomic weight and density, and v_p and v_s are compressional and shear seismic wave velocities. With the constants thus determined, regressive calculations were made and the results are shown in Table 6 and Figure 3, together with extrapolated results at high temperatures. We discussed application of the present results to Earth's interior in companion papers: *Mayama et al.*, [2004a; b].

Acknowledgements

We thank to T. Saito, I. Ohno, T. Katsura and A. Yoneda.

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Table 4. continued

γ -phase						
T/K	${}_0T_2$	${}_0S_2$	${}_1S_1$	${}_0T_3$	${}_0S_3$	${}_0S_0$
heating						
300	2457.0	2595.1	3337.1	3796.1	3847.1	4243.4
320	2453.8	2592.1	3333.5	3793.1	3842.5	4239.6
340	2451.3	2589.7	3329.5	3789.3	3838.7	4234.6
360	2448.5	2586.9	3326.1	3785.3	3834.9	4230.8
380	2446.0	2583.9	3322.3	3781.7	3830.5	4227.0
400	2442.6	2580.5	3319.1	3778.3	3826.5	4223.0
420	2439.2	2577.3	3314.5	3773.7	3821.1	4219.0
440	2436.0	2573.9	3310.7	3769.9	3815.5	4214.2
460	2432.4	2569.7	3306.5	n.d.	3809.9	4210.4
470	2430.9	2568.1	3304.5	n.d.	3807.5	4207.0
cooling from 470 K						
300	2457.1	2594.9	3336.9	3796.7	3846.9	4244.2
320	2454.6	2592.5	3333.5	3793.3	3843.1	4239.4
340	2451.4	2589.7	3329.5	3789.1	3838.9	4234.6
360	2448.6	2586.7	3325.9	3785.5	3834.5	4230.6
380	2445.8	2583.7	3322.3	3781.9	3830.3	4227.0
400	2442.3	2580.1	3319.1	3778.5	3825.7	4223.0
420	2439.7	2577.5	3314.7	3774.3	3821.3	4219.2
440	2436.8	2574.5	3310.9	3770.5	3816.3	4214.4
460	2432.9	2570.3	3306.7	n.d.	3810.7	4210.2
n.d. : no data						

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Table 5. Temperature dependence of elastic moduli of the β - and γ -phases.

β -phase				
T/K	K_S/GPa	error	μ/GPa	error
heating				
297	165.72	0.06	105.43	0.02
300	165.68	0.06	105.40	0.02
310	165.52	0.05	105.24	0.01
320	165.35	0.04	105.09	0.01
330	165.17	0.03	104.95	0.01
340	165.03	0.05	104.80	0.02
350	164.85	0.04	104.63	0.01
360	164.69	0.06	104.46	0.02
370	164.48	0.08	104.35	0.02
380	164.34	0.04	104.19	0.01
390	164.19	0.07	104.01	0.02
400	164.02	0.06	103.86	0.02
410	163.85	0.07	103.71	0.02
420	163.60	0.07	103.51	0.02
430	163.43	0.06	103.35	0.02
440	163.22	0.05	103.16	0.01
450	163.06	0.04	103.00	0.01
460	162.86	0.04	102.85	0.01
470	162.70	0.06	102.71	0.02
cooling from 470 K				
300	165.73	0.04	105.43	0.01
310	165.45	0.03	105.21	0.01
330	165.19	0.04	104.95	0.01
350	164.83	0.02	104.63	0.01
370	164.50	0.06	104.36	0.02
390	164.22	0.07	104.01	0.02
410	163.85	0.07	103.73	0.02
430	163.44	0.07	103.38	0.02
450	163.08	0.03	103.01	0.01
470	162.70	0.06	102.71	0.02

Table 5. continued

γ -phase				
T/K	K_S/GPa	error	μ/GPa	error
heating				
300	185.11	0.16	118.27	0.06
320	184.75	0.14	117.99	0.05
340	184.27	0.14	117.74	0.05
360	183.92	0.16	117.47	0.06
380	183.57	0.14	117.21	0.05
400	183.20	0.15	116.93	0.05
420	182.83	0.15	116.60	0.05
440	182.39	0.13	116.29	0.05
460	182.08	0.15	115.90	0.06
470	181.76	0.14	115.75	0.06
cooling from 470 K				
300	185.17	0.14	118.27	0.05
320	184.72	0.14	118.03	0.05
340	184.27	0.15	117.74	0.06
360	183.90	0.14	117.47	0.05
380	183.57	0.14	117.20	0.05
400	183.21	0.13	116.91	0.05
420	182.84	0.14	116.63	0.05
440	182.40	0.13	116.34	0.05
460	182.04	0.15	115.95	0.07
470	181.76	0.14	115.75	0.06

 K_S : adiabatic bulk modulus μ : shear modulusTable 6. Regressive values of the elastic moduli and their extrapolation to lower and higher temperatures using the modified-Wachtman's equation, $M(T)=M_0-gE(\theta,T)$. The M_0 and g were determined by the least squares calculation giving the values $\theta_{ac}=841$ and 884 K to the θ of the β - and γ -phases, respectively.

T/K	β -phase		γ -phase	
	K_S/GPa	μ/GPa	K_S/GPa	μ/GPa
50	167.7	107.3	187.2	119.9
100	167.7	107.2	187.1	119.9
150	167.4	107.0	186.9	119.7
200	167.0	106.6	186.5	119.4
250	166.4	106.0	185.8	118.9
298	165.7	105.4	185.1	118.3
300	165.7	105.4	185.0	118.3
350	164.9	104.6	184.2	117.6
400	164.0	103.9	183.2	116.9
450	163.1	103.0	182.2	116.1
500	162.1	102.2	181.2	115.3
550	161.1	101.3	180.1	114.5
600	160.1	100.4	179.0	113.6
650	159.1	99.4	177.8	112.8
700	158.1	98.5	176.7	111.9
750	157.0	97.6	175.6	111.0
800	156.0	96.6	174.4	110.1
900	153.9	94.7	172.0	108.3
1000	151.7	92.7	169.7	106.5
1100	149.6	90.8	167.3	104.6
1200	147.4	88.8	164.9	102.8
1300	145.2	86.9	162.4	100.9
1400	143.1	84.9	160.0	99.1
1500	140.9	82.9	157.6	97.2
1600	138.7	80.9	155.1	95.3
1700	136.5	78.9	152.7	93.4
1800	134.3	76.9	150.2	91.6
1900	132.1	74.9	147.8	89.7
2000	129.9	72.9	145.3	87.8
2100	127.7	70.9	142.9	85.9
2200	125.5	68.9	140.4	84.0
$M_0/\text{GPa}=\$	169.7	108.0	187.2	108.0
$g/\text{Mmol m}^{-3}=\$	0.89	0.81	0.99	0.76

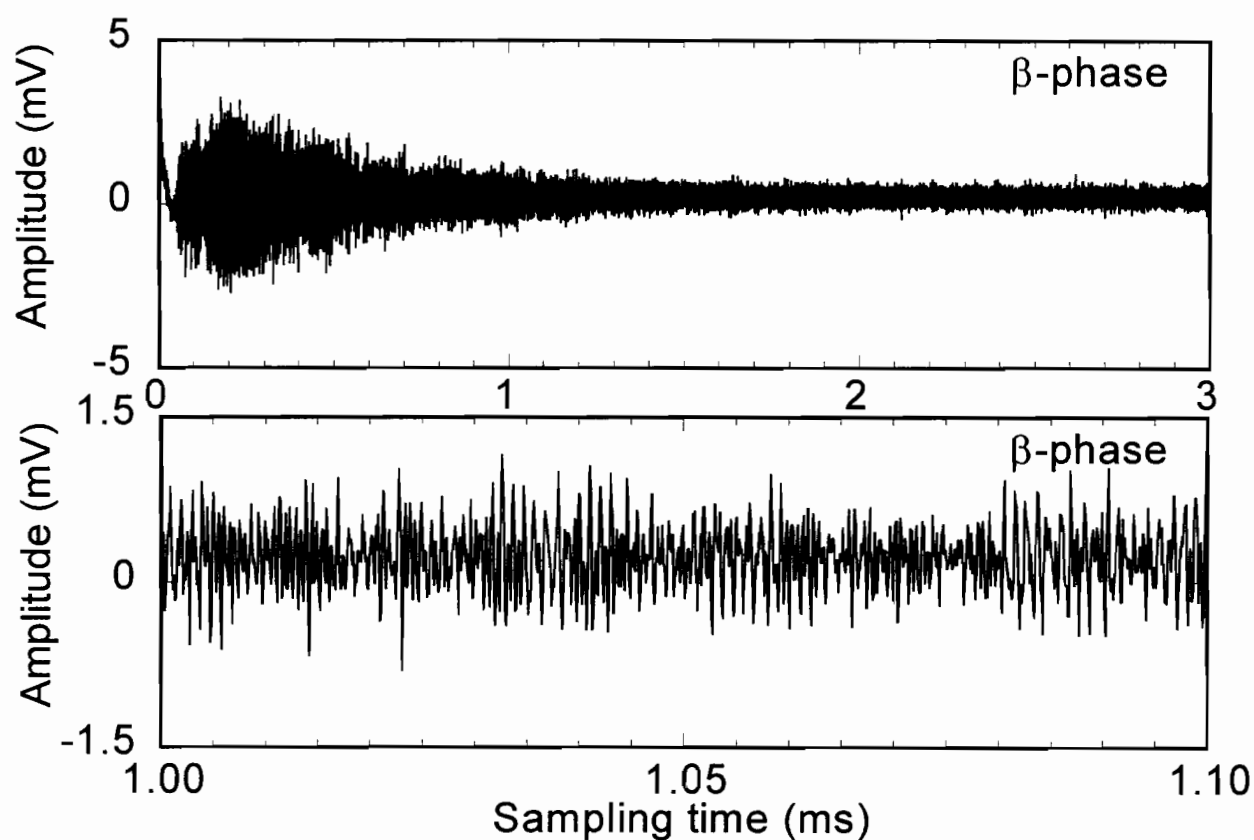


Figure 1-A. The averaged waveform of the β -phase specimen at 320 K. Partly enlarged at the bottom panel.

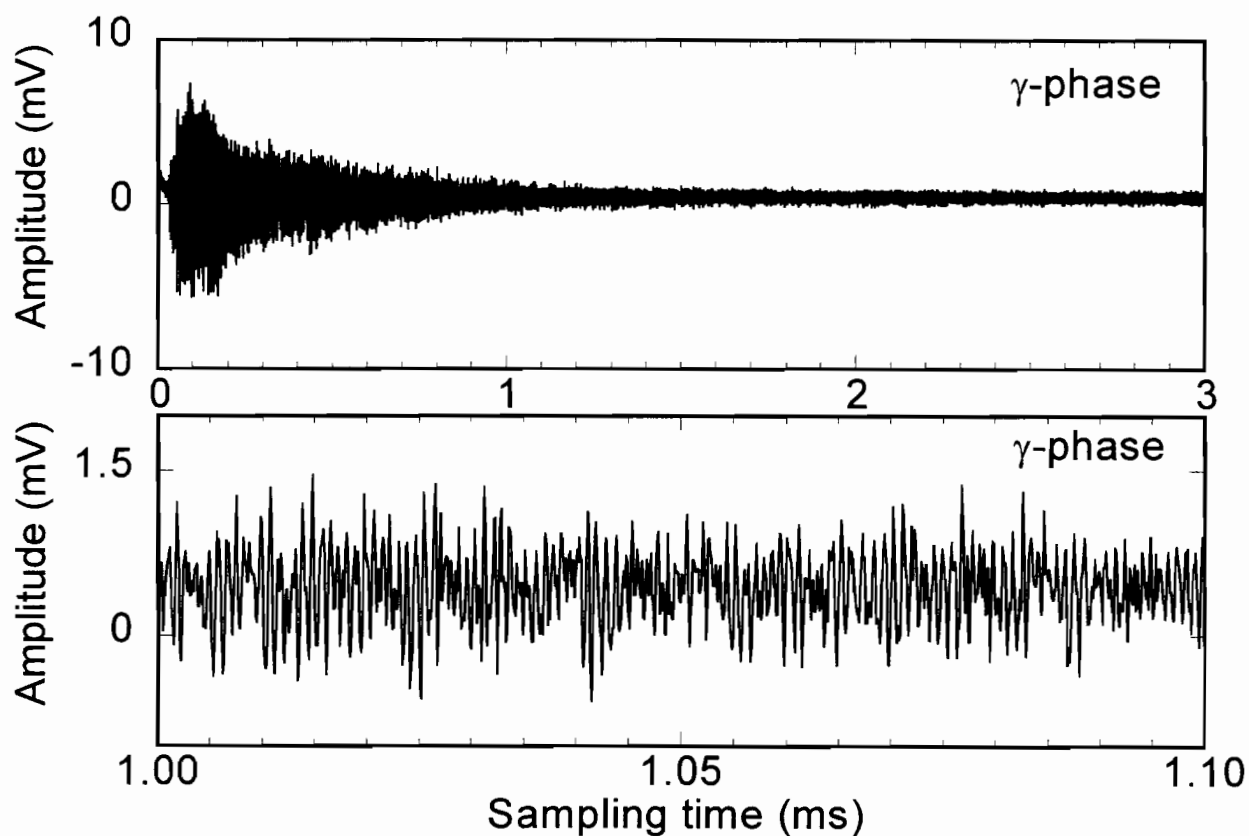


Figure 1-B. The averaged waveform of the γ -phase specimen at 320 K. Partly enlarged at the bottom panel.

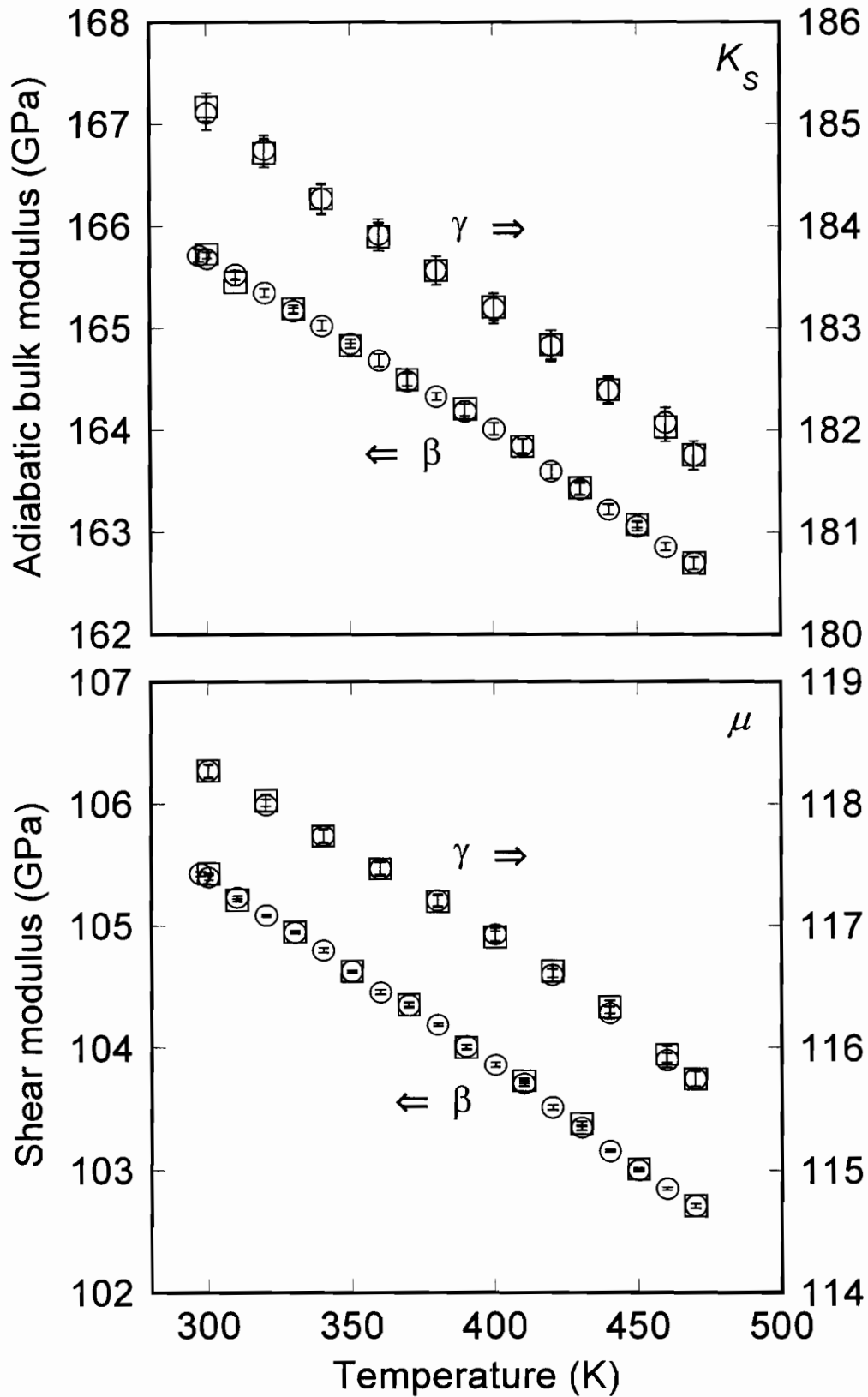


Figure 2. Temperature dependence of elastic moduli of the β - and γ -phases. Error bars represent the probable error. Open circles and squares represent heating and cooling processes, respectively.

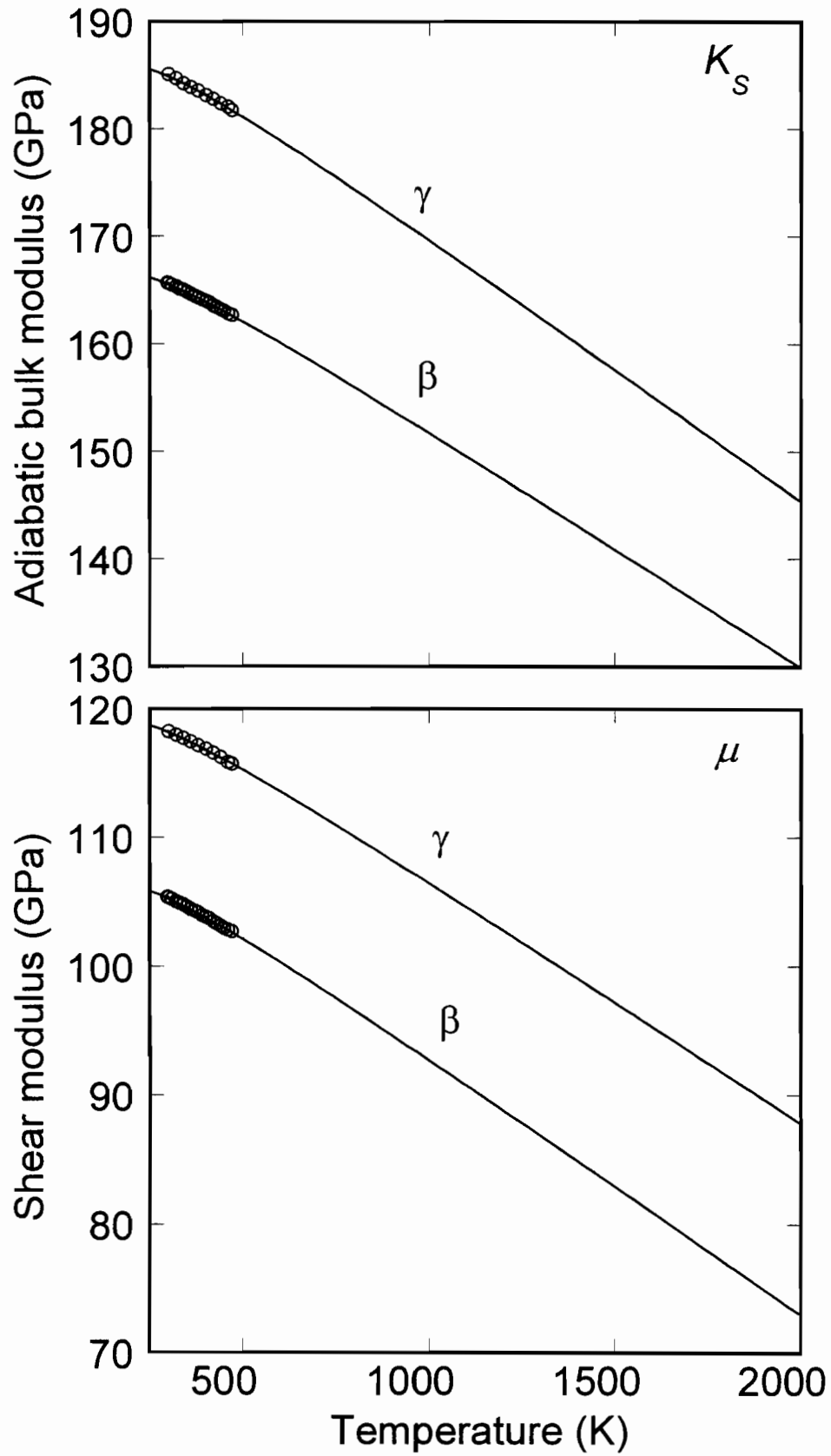


Figure 3. Temperature dependence of elastic moduli of the β - and γ -phases. Regressive calculation (open circle) and their extrapolation to lower and higher temperatures (solid curve).