

THERMAL EXPANSION OF SINGLE-CRYSTAL MANGANOSITE

Isao SUZUKI, Shin-ichi OKAJIMA,* and Kiyoshi SEYA

*Department of Earth Sciences, Faculty of Science,
Okayama University, Okayama, Japan*

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Thermal expansion of manganosite MnO at temperatures between 20°C and 850°C has been carefully determined by a dilatometric technique. The theory of thermal expansion by Grüneisen is improved and the acquired data are analyzed to derive the harmonic and anharmonic parameters of MnO. Grüneisen's parameter γ is 1.56, Debye temperature is 441 K, and pressure derivative of bulk modulus is 7. The volume expansion coefficient is $34.3 \times 10^{-6}/\text{K}$ at 20°C and $47.1 \times 10^{-6}/\text{K}$ at 850°C; almost the same in magnitude to those of MgO and FeO.

1. Introduction

We have been studying the thermal properties of the materials composing the earth's mantle and their related compounds. Subsequent to the latest measurement on tephroite Mn_2SiO_4 (OKAJIMA *et al.*, 1978), the thermal expansion of manganosite MnO, the manganese analogue to periclase MgO and wüstite FeO, was determined up to 850°C, to obtain a better understanding of the anharmonic properties of these materials.

The useful information on the anharmonic property of a solid is derived by an appropriate analysis of accurate thermal expansion data (WACHTMAN *et al.*, 1962; SUZUKI, 1975). The usual practice is the application of Grüneisen's theory of thermal expansion with some approximation. In this paper, an improved expression of thermal strain, in which the second order term is exactly included, is proposed and comparison of the analyzed result with that by the previous method is made on the manganosite data.

2. Sample and Experimental Procedure

A single-crystal manganosite grown by a flame fusion technique was afforded by Nakazumi Crystal Co. This specimen is glossy and black, but neither crack nor flaw is found penetrating into the interior of the specimen.

* Present address: Nippon Geophysical Prospecting Co., Ltd, 12-2, 2-chome, Nakamagome, Ohta-ku, Tokyo, Japan.

Table 1. Observed and calculated values of thermal expansion and its coefficient for manganosite MnO.

Temp.	Observed expansion	Calculated expansion and its coefficient			
		Linear		Volume	
t °C	Y_L 10 ⁻²	Y_L 10 ⁻²	α_L 10 ⁻⁶ K ⁻¹	Y_V 10 ⁻²	α_V 10 ⁻⁶ K ⁻¹
-200		-0.1950	3.3	-0.5837	9.8
-150		-0.1685	7.1	-0.5046	21.2
-100		-0.1272	9.3	-0.3812	27.7
-50		-0.0777	10.5	-0.2330	31.4
0		-0.0234	11.2	-0.0702	33.7
20	0.0	-0.0008	11.4	-0.0023	34.3
25	0.0045	0.0050	11.5	0.0149	34.5
50	0.0328	0.0340	11.7	0.1021	35.2
75	0.0630				
100	0.0942	0.0937	12.1	0.2814	36.3
125	0.1249				
150	0.1564	0.1551	12.4	0.4661	37.3
175	0.1870				
200	0.2187	0.2180	12.7	0.6556	38.1
225	0.2497				
250	0.2818	0.2823	12.9	0.8492	38.8
275	0.3138				
300	0.3474	0.3477	13.2	1.047	39.5
325	0.3807				
350	0.4143	0.4142	13.4	1.248	40.1
375	0.4467				
400	0.4821	0.4819	13.6	1.453	40.7
425	0.5160				
450	0.5503	0.5507	13.8	1.661	41.4
475	0.5863				
500	0.6199	0.6205	14.0	1.873	42.0
525	0.6567				
550	0.6918	0.6916	14.2	2.089	42.7
575	0.7275				
600	0.7634	0.7637	14.4	2.309	43.3
625	0.8006				
650	0.8376	0.8371	14.7	2.532	44.0
675	0.8743				
700	0.9112	0.9117	14.9	2.760	44.7
725	0.9495				
750	0.9884	0.9876	15.2	2.992	45.5
775	1.027				
800	1.064	1.065	15.4	3.229	46.3
825	1.104				
850	1.144	1.144	15.7	3.470	47.1
900		1.224	16.0	3.716	48.0
950		1.306	16.3	3.968	48.9
1,000		1.389	16.6	4.225	49.9
1,050		1.474	17.0	4.488	51.0
1,100		1.561	17.4	4.758	52.1
1,150		1.651	17.8	5.034	53.3
1,200		1.742	18.2	5.318	54.6
1,250		1.836	18.7	5.609	56.0
1,300		1.932	19.2	5.910	57.6
1,350		2.032	19.8	6.219	59.3
1,400		2.134	20.4	6.540	61.2

This crystal was shaped into a cylinder along $\{1\ 0\ 0\}$ axis about 7 mm in height, and both ends of the cylinder were polished to be parallel. Bulk density determined from the size and mass of the specimen is 5.373 ± 0.011 g/cm³ at 20°C.

The experimental technique and apparatus to measure thermal expansion were reported in previous papers (SUZUKI, 1975; OKAJIMA *et al.*, 1978). By using a 10:10:1 mixture of CO₂, Ar, and H₂ gasses, the oxygen partial pressure of the specimen environment was brought to the order of 10^{-16} bar at 850°C. The specimen after the measurement did not show any evidence of alteration. The acquired data of the thermal expansion are shown in the second column of Table 1.

3. Theoretical Representation of Thermal Expansion

In the previous work, the following theoretical expression of thermal expansion was used for the analysis of data (GRÜNEISEN, 1926; SUZUKI, 1975);

$$\begin{aligned} y_v(T) &= (V(T) - V(0))/V(0) \\ &= E(\theta, T)/(Q_0 - kE(\theta, T)) \end{aligned} \quad (1)$$

where $y_v(T)$ is relative volume expansion at temperature T referred to 0 K, V is the volume, $E(\theta, T)$ is the thermal energy as a function of T , and θ is the Debye temperature θ . $Q_0 (\gg kE)$ is such a quantity that determines the magnitude of thermal expansion, and is defined by

$$Q_0 = B_0 \cdot V_0 / \gamma$$

where γ is Grüneisen's parameter, B_0 and V_0 are bulk modulus and volume at 0 K. k is also an anharmonic parameter related to the pressure derivative of bulk modulus dB_0/dP at 0 K;

$$k = (dB_0/dP - 1)/2.$$

The thermal expansion in Eq. (1) referred to 0 K, is converted to that referred to a reference temperature T_r ,

$$\begin{aligned} Y_v(T) &= y_v(T)/a_v + (1 - a_v)/a_v \\ &= E(\theta, T)/a_v(Q_0 - kE(\theta, T)) + (1 - a_v)/a_v \end{aligned} \quad (2)$$

where a_v is the ratio of volumes at T_r and 0 K, i.e., $a_v = V(T_r)/V(0)$. The volume expansion is related to linear expansion defined by $Y_L(T) = (L(T) - L(T_r))/L(T_r)$, where $L(T)$ is a linear dimension of the crystal; thus,

$$Y_v(T) = 3Y_L(T) + 3Y_L^2(T) + Y_L^3(T). \quad (3)$$

Then Eq. (2) can also be represented in terms of linear expansion. The approximate expression which have been employed (WACHTMAN *et al.*, 1962) is

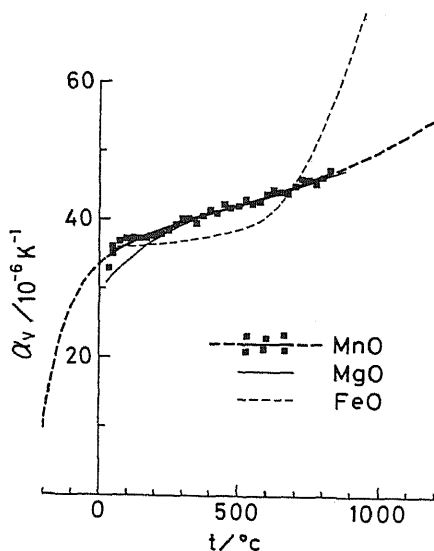


Fig. 1. Observed and calculated values of volume expansion coefficient α_v of manganosite MnO. α_v is extrapolated over wider range of temperature by Eq. (6). α_v of periclase MgO (SUZUKI, 1975) and of polycrystalline wüstite Fe_{1-x}O (CARTER, 1959) are compared.

based on the first term alone of Eq. (3); so that,

$$Y_L(T) = E(\theta, T) / [3a_L(Q_0 - kE(\theta, T))] + (1 - a_L) / a_L \quad (4)$$

where a_L is the ratio of linear dimensions at T_r and 0 K, i.e., $a_L = L(T_r) / L(0) = a_v^{1/3}$. In fitting Eq. (2) or Eq. (4) to the experimental data, a_v or a_L is an additional parameter to be determined.

The procedure in the derivation of Eq. (1) is as follows; 1) the Taylor expansion of the potential term in the Mie-Grüneisen equation of state is terminated at the first order, and 2) the additional second order term is approximated from the first order term by way of iteration (see SUZUKI, 1975, for detail). Because of the approximate treatment of the second order term of $y_v(T)$ in Eq. (1), the constants Q_0 , θ , and k to be determined may be systematically biased. Further, the conversion of Eq. (2) to Eq. (4) involves the approximation $Y_v(T) = 3Y_L(T)$, which would also lead to the numerical difference of Q_0 , θ and k depending on the way of analysis, namely, fitting by linear expansion or by volume expansion.

Yet, the approximations in deriving Eqs. (1) and (4) have scarcely given rise to any problem, since the accuracy of thermal expansion measurement has not been sufficiently high. If, however, we are to derive more information from more accurate data, the exact treatment of Grüneisen's theory and

an accurate conversion of volume and linear expansions should be made. When we take account of the contribution of the second order term of Grüneisen's theory exactly, we have to solve the quadratic equation

$$ky_v - y_v^2 + E(\theta, T)/Q_0 = 0$$

whose solution is

$$y_v(T) = (1 - \sqrt{1 - 4kE(\theta, T)/Q_0})/2k. \quad (5)$$

This equation has the same parameters as Eq. (1). Volume expansion referred to a reference temperature T_r is thus represented by

$$Y_v(T) = (1 + 2k - \sqrt{1 - 4kE(\theta, T)/Q_0})/2ka_v - 1. \quad (6)$$

By using the exact relation; $1 + Y_v(T) = (1 + Y_L(T))^3$, we have

$$Y_L(T) = (1 + 1/2k - \sqrt{1 - 4kE(\theta, T)/Q_0}/2k)^{1/3}/a_L - 1. \quad (7)$$

Equation (7) is certainly more complicated but more rigorous than Eq. (4) given by WACHTMAN *et al.* (1962). The complicated expression of the equation is not, however, a matter of any difficulty with the practical data analysis with a computer.

4. Results of Data Analysis

Calculations based on the least squares method using Eqs. (2), (4), (6), and (7) were made with the aid of an iteration technique to determine the numerical parameters; Q_0 , θ , k , and a 's from the present data of manganosite. These parameters having been determined, their probable errors, and standard deviations are listed in Table 2. The standard deviations are equally small of the order of 10^{-5} (the last column in Table 2), indicating that the previous Eqs. (2) and (4) are as good as the proposed new Eqs. (6) and (7) in fitting the experimental data. However, the value of k determined by volume expansion (Eq. (2)) and by linear expansion (Eq. (4)) are significantly different, while the same value of k is derived in the proposed Eqs. (6) and (7) as

Table 2. Comparison of expansion parameters in Eqs. (2), (4), (6), and (7) for manganosite MnO.

	$\frac{Q_0}{10^6 \text{ J/mol}}$	$\frac{\theta}{K}$	k	$\frac{a^1 - 1}{10^{-2}}$	$\frac{\sigma^2}{10^{-4}}$
Eq. (2)	1.403 ± 0.008	359 ± 18	4.20 ± 0.08	0.661 ± 0.014	0.19
Eq. (4)	1.403 ± 0.008	359 ± 18	3.88 ± 0.08	0.220 ± 0.005	0.06
Eq. (6)	1.343 ± 0.005	441 ± 13	3.03 ± 0.04	0.608 ± 0.010	0.19
Eq. (7)	1.343 ± 0.005	441 ± 13	3.03 ± 0.04	0.202 ± 0.003	0.06

¹⁾ Reference temperature 20°C, $a = a_v$ for Eqs. (2) and (6), $a = a_L$ for Eqs. (4) and (7).

²⁾ $\sigma = \{\sum (Y_{\text{obs}} - Y_{\text{calc}})^2 / (n - q)\}^{1/2}$, n , number of input data; q , number of parameters to be determined.

a matter of course. Further, the probable errors of Q_0 , θ , k , and a obtained by Eqs. (6) and (7) are certainly less than those by Eqs. (2) and (4). Therefore, it is concluded that Eq. (6) or Eq. (7) is definitely better than Eqs. (2) and (4). The systematic deviation of Q_0 , θ , k , and a by the application of Eqs. (2) and (4) has been clarified as shown in Table 2. It is stressed that the second order term of strain should be taken into account in order to achieve a reliable analysis of data.

In Table 1, the observed linear expansion Y_L of manganosite is compared with that calculated by Eq. (7) with the parameters listed in Table 2. The volume expansion Y_V and expansion coefficient α are calculated over a wider range of temperature by Eq. (6) and are shown in Table 1.

5. Discussion

The volume expansion coefficient of MnO is compared with those of periclase (SUZUKI, 1975) and wüstite (CARTER, 1959) in Fig. 1. These oxides have almost the same magnitude of expansion coefficients in the temperature range of measurement. A noticeable feature in wüstite is the steep increase of the expansion coefficient above 600°C. There are several possible causes: 1) wüstite is not stable below 560°C (CARTER, 1959), 2) the change of stoichiometry (vacancy concentration) with temperature and partial pressure of oxygen (DARKEN and GURRY, 1946), 3) the changes of structure and of the associated defects in Carter's polycrystalline specimen, and/or 4) the effect of magnetic transition (Néel temperature $T_N = -84^\circ\text{C}$; BOZORTH *et al.*, 1972). The second and third possibilities are most likely, but the discussion should be reserved until the specified data on the single-crystalline sample is worked out. The last effect may also be present in MnO ($T_N = -153^\circ\text{C}$; BOZORTH *et al.*, 1972), but the transition temperature is too low to affect significantly the properties of MnO at high temperature.

The similarity of thermal expansion coefficients in MgO, FeO and MnO suggests that rock-salt oxides relevant to the earth's mantle show essentially the same thermal expansion coefficient; 35 at room temperature and 50 at 1,000°C in the unit of $10^{-6}/\text{K}$. Above the Debye temperatures, these oxides show an expansion coefficient about a quarter smaller than those of the typical ionic crystals such as alkali-halides with rock-salt structure (KIRBY *et al.*, 1972). This fact is understood by comparing the valence product ($2 \times 2 = 4$) of the divalent compounds and that ($1 \times 1 = 1$) of monovalent alkali-halides.

The harmonic and anharmonic parameters from the present expansion measurement are compared with those derived from other sources. Debye temperature calculated by the elastic wave velocities of MnO (Sumino, personal communication, 1978) is $\theta = 537$ K. The characteristic temperature

441 K derived from Eq. (6) or Eq. (7) is smaller by 100 K than the acoustic Debye temperature. The source of this discrepancy is not yet understood. It is noted that the characteristic temperature 359 K derived by an application of the previous Eq. (2) or Eq. (4) is too small. This may be another reason for supporting the use of Eqs. (6) and (7) instead of Eqs. (2) and (4). The value of k ($= (dB_0/dP - 1)/2$) gives the pressure derivative of bulk modulus $dB_0/dP = 7.0$, which is not an unreasonable magnitude when compared with $\partial B/\partial P$ of ordinary solid materials. The lattice parameter of manganosite at 25°C is given as 4.4448 Å (ROBIE *et al.*, 1966). By using the values of a from Eq. (6) or Eq. (7) in Table 2, the lattice constant and molar volume of manganosite at 0 K are given as 4.4358 ± 0.0005 Å and 13.140 ± 0.005 cm³/mol. By combining the values of $Q_0 = 1.34 \times 10^6$ J/mol and $B_0 \cdot V_0 = 2.095 \times 10^6$ J/mol (approximated from the room temperature data), we get Grüneisen's parameter γ ($\cong B \cdot V/Q_0$) $\cong 1.56$. This γ is theoretically different from the thermal Grüneisen's parameter γ_{th} , but the numerical difference may be very small, a few percent at most (SUZUKI and KUMAZAWA, 1978).

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