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ORIGINAL PAPER

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The elastic constants of monoclinic single-crystal chrome-diopside to 1,300 K

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Abstract Values of the complete adiabatic elastic tensor for single-crystal chrome-diopside (a monoclinic pyroxene mineral) are presented from 298 to 1,300 K. The data were obtained using resonant ultrasound spectroscopy (RUS). They are the first published results for the temperature *T* dependences of the 13 individual elastic constants C_{ij} of any clinopyroxene mineral. Each C_{ij} is appropriately described by a linear function in *T* throughout the range of *T*. Values for each $(\partial C_{ij}/\partial T)_P$ in GPa K^{-1} are as follows: C_{11}, −0.0291; C_{22}, −0.0248; C_{33}, −0.0179; C_{44}, −0.0103; C_{55}, −0.0077; C_{66}, −0.0152; C_{12}, −0.0119; C_{13}, −0.0064; C_{23}, 0.0000; C_{15}, 0.0025; C_{25}, 0.0022; C_{35}, −0.0046; and C_{46}, 0.0026. Values of $(\partial M/\partial T)_P$ in GPa K^{-1}, where *M* represents an isotropic bulk property calculated from the C_{ij} data, are as follows: adiabatic bulk modulus K_S, −0.0123; isothermal bulk modulus K_T, −0.0178; and shear modulus *G*, −0.00998. Some diopside derivatives, notably $(\partial K_S/\partial T)_P$, $(\partial K_T/\partial T)_P$, and $(\partial V_P/\partial T)_P$, where V_P is the compressional wave velocity, have smaller magnitudes than all other minerals of importance in Earth's mantle, thus, confirming predictions from systematics studies. We find several dimensionless quantities for this monoclinic mineral have normal values compared to other mantle minerals. Further, αK_T (α is the volume coefficient of thermal expansion) for diopside is approximately independent of both *T* and volume *V* at elevated temperature, so its equation of state is accurately expressed in simplified form.

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Introduction

Knowledge of the elastic properties of candidate mantle minerals, and how these properties vary with temperature *T* and pressure *P*, are required to develop reliable compositional models of Earth's mantle. The four main minerals of Earth's upper mantle are generally believed to be olivine, orthopyroxene, clinopyroxene, and garnet; albeit, different models ascribe varying amounts of these minerals to the upper mantle. Pyrolitic compositional models [see, e.g., Green and Falloon (1998) or Jackson and Rigden (1998)], with olivine content near 60%, generally require 10% clinopyroxene by volume at the 410-km discontinuties, and significantly more at shallower depths (Duffy and Anderson 1989; Agee 1998). Several studies, however, have arrived at different conclusions regarding the olivine content of Earth's upper mantle (Bass and Anderson 1984; Bina and Wood 1987; Weidner and Ito 1987; Duffy and Anderson 1989; Gwanmesia et al. 1990; Ita and Stixrude 1992; Duffy et al. 1995; Li et al. 1998, 2001). Some of these studies support an olivine component in the upper mantle near, and even below, 40%, in which case the clinopyroxene content is at least 37% at 410 km (Duffy and Anderson 1989) and more at shallower depths. Irrespective of what compositional model of Earth's upper mantle is assumed, it is clear that clinopyroxene is an important mantle mineral and knowledge of its elastic properties represents an important component of the upper mantle mineralogic database.

Diopside ($CaMgSi_2O_6$), enriched in Cr, is a representative clinopyroxene in the upper mantle and is the clinopyroxene typically found in peridotite (MacDonough and Rudnick 1998). Early acoustic work to determine the elasticity of diopside was done by Aleksandrov et al. (1964) and Liebermann and Mayson (1976).

Aleksandrov et al. (1964) reported values at ambient P and T for the second-order adiabatic elastic tensor C_{ij} of single-crystal diopside; Liebermann and Mayson (1976) reported results on the isotropic moduli from ultrasonic measurements on a hot-pressed specimen, also at ambient conditions. Levien et al. (1979) measured the single-crystal C_{ij} of a natural, near end-member diopside using Brillouin spectrsocopy. Levien et al. (1979) note several peculiarities in the report by Aleksandrov et al. (1964), including the prospect of heterogeneities and inclusions in the sample and the likelihood that it was misoriented. Nevertheless, the final value for the adiabatic bulk modulus K_S found by Aleksandrov et al. (1964) is close to that of Levien et al. (1979); whereas, the Aleksandrov et al. (1964) shear modulus is about 10% higher than was found by Levien et al. (1979). Levien et al. (1979) also performed an X-ray study under pressure in a diamond cell to determine the diopside $K_T' \equiv (\partial K_T/\partial P)_T$, where K_T is the isothermal bulk modulus. The K_T' value reported by Levien et al. (1979) was adjusted by Levien and Prewitt (1981) in a reanalysis of the original Levien et al. data. More recently, Bhagat et al. (1992) measured the C_{ij} of an omphacite with composition on the jadeite side of the jadeite–diopside join, and Collins and Brown (1998) reported C_{ij} data for a natural clinopyroxene with a significant diopside component (72%). Finally, Isaak and Ohno (2003) reported the first set of C_{ij} for a monoclinic material using resonant ultrasound spectroscopy (RUS) in their study of chrome-diopside at ambient T.

To date, however, there are no data on the T dependences of elasticity of single-crystal diopside, or any other clinopyroxene mineral. This gap in the database is due in large part to complexities in working with the low-symmetry monoclinic crystal structures of such materials. Thus, in compositional models of Earth's upper mantle, the T dependences of clinopyroxene must be guessed at (Weidner and Ito 1987) or estimated from velocity systematics (Duffy and Anderson 1989; Agee 1998). Systematic studies have proven to be powerful tools in studying material properties (Anderson 1988; Duffy and Anderson 1989). The difficulty with systematics, however, is that there is no guarantee material properties of unmeasured systems will follow established patterns. For example, the unusually high value of the P derivative of the bulk modulus in orthopyroxene (Frisillo and Barsch 1972; Angel and Hugh-Jones 1994; Flesch et al. 1998; Angel and Jackson 2002) does not appear to be reconcilable with the K_T'-ρ (ρ is the density) systematics determined from other mantle minerals. Thus, one cannot be certain of the conclusions when using systematics to predict values of unmeasured parameters; experimental data are required to provide this certainty.

We present data on the T dependences for the 13 independent elastic constants C_{ij} of a natural chrome-diopside single-crystal. These data are all at ambient P. To our knowledge, they represent the first set of C_{ij} data reported for any clinopyroxene mineral at elevated T.

Experimental procedures

The complete second-order adiabatic elastic constant tensor C_{ij} for single-crystal chrome-diopside was determined to 1,300 K using RUS. We used the right-rectangular parallelepiped resonance (RPR) version of RUS. In RPR, the C_{ij} of an oriented right-rectangular parallelepiped specimen are determined from measurements of the resonance spectrum, edge lengths, and density. The theory of RPR applied to monoclinic crystals is presented by Isaak and Ohno (2003), who also demonstrated its application at ambient P and T by obtaining the 13 independent C_{ij} of a gem quality single-crystal chrome-diopside specimen. In the current report, we extend the measurements and analysis on this same specimen to high T.

As described by Isaak and Ohno (2003), the measured specimen density at room T is 3.286 ± 0.005 g cm^{-3}, consistent with density estimates from end member components. The specimen composition is $Di_{0.93}Hd_{0.03}Ur_{0.02}X_{0.02}$, where Di, Hd, and Ur indicate diopside $CaMgSi_2O_6$, hedenbergite $CaFe^{+2}Si_2O_6$, and ureyite $NaCrSi_2O_6$, respectively, and X represents all other minor components. The prepared right-rectangular parallelepiped specimen has edge lengths of 4.169 ± 0.003 and 4.905 ± 0.006 mm along the respective [010] and [001] axes. The third edge has a length of 4.749 ± 0.002 mm and is perpendicular to the two axes cited above. To be sure, this third edge (herein referred to be along the A axis, with capital intentional) is normal to the (100) plane, but is not along [100] axis.

The specimen density and edge lengths must be specified at each T when performing high-T data reduction. We used the average of the Cameron et al. (1973) and Finger and Ohashi (1976) thermal expansion data for diopside to account for changes in the specimen edge lengths and density at each T. The calculated C_{ij} at high T are not very sensitive to the exact choice of thermal expansion values used. We also used the Cameron et al. (1973) and Finger and Ohashi (1976) thermal expansion data to determine if the prepared specimen retains three pairs of mutually orthogonal planes at high T, since the data reduction scheme assumes right-rectangular parallelepiped geometry at each T. Our particular concern was whether the A axis remains orthogonal to the [010] axis at high T. We find these axes deviate by 0.2–0.4° from orthogonality at 1,300 K, if they are perfectly orthogonal at room T. This deviation is less than the uncertainty of ±1° with which the prepared specimen is originally oriented and is, therefore, not further considered in our analysis.

Frequency data were acquired in the range of 300–1,500 kHz. Figure 1 illustrates the T dependence of part of the observed spectrum. Frequency scans were performed at room T (298 K), 325 K, and then in

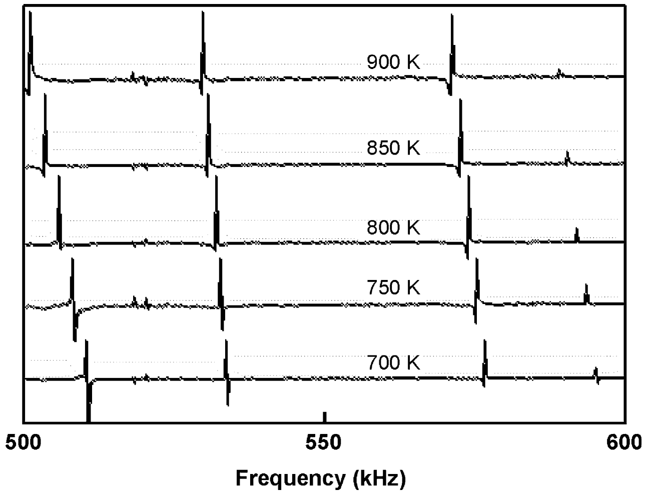

Fig. 1 Samples of resonance spectra of chrome-diopside showing the T variation of four modes from 700 to 900 K

increments of 25° up to 950 K. From 950 to 1,300 K, increments of 50° were used. Temperature was measured with two Pt–Pt13%Rh thermocouples placed on opposite sides of the specimen. The uncertainty in T is estimated at ±4° at the highest T. In order to observe and track as many modal frequencies as possible, we made several temperature excursions, including runs to 900, 950, and 2–1300 K. Several of the same modes were observed on each excursion. We found excellent reproducibility in the measured T dependences of modes for which redundant T data were obtained.

In presenting the RPR theory for crystals with monoclinic symmetry, Isaak and Ohno (2003) used the first 62 modal frequencies to constrain the 13 independent C_{ij} at room T. However, when making high T measurements, alumina buffer rods are required to remove the transducers from direct contact with the hot specimen (Goto and Anderson 1988; Isaak et al. 1989). Thus, the resonant signal strength is reduced, and some modes are not readily observed. We observed 39 of the lowest 62 modal frequencies over the entire T range studied and used these 39 modes to identify the T dependences of the C_{ij}.

The room-temperature C_{ij} values determined with the 39 modes were referenced to those reported by Isaak and Ohno (2003) based on all of the 62 lowest modal frequencies. There is a small mismatch in room-temperature C_{ij} when comparing between values determined from the 39- and 62-modal frequency data sets (see first numeric column of Table 1). The discrepancy is slight, amounting to less than 1.0 GPa for each C_{ij}, except for C_{33}. For C_{33}, the difference is slightly larger than 1.0 GPa; we obtained 244.2 GPa for C_{33} using 39 modes, compared to 245.4 GPa reported by Isaak and Ohno (2003) using all 62 modes. The difference of 1.2 GPa (or 0.5%) is within the uncertainty cited by Isaak and Ohno (2003). We adjusted the C_{ij} determined from the 39-mode data set at each T by applying the same small amount required to bring the room-temperature

Table 1 Temperature dependences of single-crystal and aggregate elastic moduli for chrome-diopside (clinopyroxene) and bronzite (orthopyroxene)

Modulus (M)	Chrome-diopside[a]		Bronzite[b]	
	Value at 298 K[c]	$(\partial M/\partial T)_P^d$	Value at 298 K[c]	$(\partial M/\partial T)_P^d$
C_{11}	228.1 ± 1.0 (228.9)	−0.0291	228.6 ± 0.1	−0.0352 ± 0.001
C_{22}	181.1 ± 0.6 (181.4)	−0.0248	160.5 ± 0.1	−0.0328 ± 0.001
C_{33}	245.4 ± 1.3 (244.2)	−0.0179	210.4 ± 0.1	−0.0516 ± 0.004
C_{44}	78.9 ± 0.3 (79.2)	−0.0103	81.75 ± 0.09	−0.0131 ± 0.003
C_{55}	68.2 ± 0.2 (67.8)	−0.0077	75.48 ± 0.09	−0.0138 ± 0.002
C_{66}	78.1 ± 0.2 (77.9)	−0.0152	77.66 ± 0.05	−0.0145 ± 0.005
C_{12}	78.8 ± 0.5 (79.5)	−0.0119	71.0 ± 0.2	−0.0212 ± 0.007
C_{13}	70.2 ± 0.7 (70.1)	−0.0064	54.8 ± 0.2	−0.0318 ± 0.008
C_{23}	61.1 ± 0.7 (60.4)	0.0000	46.0 ± 0.2	−0.0107 ± 0.007
C_{15}	7.9 ± 0.5 (7.8)	0.0025		
C_{25}	5.9 ± 0.5 (5.3)	0.0022		
C_{35}	39.7 ± 0.4 (38.9)	−0.0046		
C_{46}	6.4 ± 0.2 (6.3)	0.0026		
K_S	116.5 ± 0.9[e] (116.6)	−0.0123	103.5	−0.0268
K_T	115.9 ± 0.9[e] (116.0)	−0.0178	98.8	−0.0296
G	72.8 ± 0.4 (72.7)	−0.00998	75.5	−0.0119
V_P	8.06 ± 0.2 (8.06)	-3.66×10^{-4}	7.78	-9.08×10^{-4}
V_S	4.71 ± 0.1 (4.70)	-2.56×10^{-4}	4.72	-4.86×10^{-4}

[a] Current results referenced to values obtained with 62 modes at 298 K; Numbers in parenthesis are unreferenced 298-K values obtained from the 39-mode data set

[b] Frisillo and Barsch (1972); $(Mg_{0.8}Fe_{0.2})SiO_3$

[c] C_{ij}, K_S, K_T, G in GPa; V_P, V_S in km s^{-1}

[d] Derivatives of Cij, K_S, K_T, G in GPa K^{-1}and of V_P, V_S in km s^{-1} K^{-1}

[e] Arithmetic average of Hashin–Shtrikman bounds

C_{ij} values into coincidence with those reported by Isaak and Ohno (2003).

Results

Results for the $C_{ij}(T)$ are illustrated in Fig. 2a–d. Uncertainties shown in these figures are propagated from possible systematic errors in length and density, and from the residuals of the fitted modal frequencies at each T. The uncertainties derived from the residuals represent about 75% of the indicated uncertainty for each C_{ij} and are discussed in more detail by Isaak and Ohno (2003). The uncertainties in the C_{15} and C_{25} moduli appear anomalously large when compared with other C_{ij}. However, this effect is due to the actual values of C_{15} and C_{25} having small magnitudes compared to other C_{ij}. The scale of Fig. 2d is expanded, relative to the other figures. To be sure, the percent error of the the C_{15} and C_{25} moduli are significantly more than the other C_{ij}.

In Fig. 2a–d, we see that each C_{ij} is appropriately described by a linear function in T throughout the range of T used. Values for each $(\partial C_{ij}/\partial T)_P$ are provided in Table 1. We also list values of $(\partial C_{ij}/\partial T)_P$ for bronzite (a type of orthopyroxene with nine independent C_{ij}) in Table 1 for comparative purposes.

Discussion

We determined the T dependences of several important material properties from the measured $C_{ij}(T)$ presented above. Figures 3 and 4 show the T dependences of some isotropic properties. In Fig. 3, we see the T dependences of the adiabatic and isothermal bulk moduli, K_S and K_T, respectively, and the rigidity modulus G. The K_S and G moduli were computed from the C_{ij} using the Hashin–Shtrikman averaging scheme for monoclinic crystals (Watt 1980). Values of K_T were then determined from K_S using the thermodynamic relation

$$K_T = \frac{K_S}{1 + \alpha\gamma T}, \tag{1}$$

where the Grüniesen parameter γ is given by

$$\gamma = \frac{\alpha K_S}{\rho C_P}. \tag{2}$$

When evaluating K_T and γ in (1) and (2), we assumed values of coefficient of thermal expansion α and heat

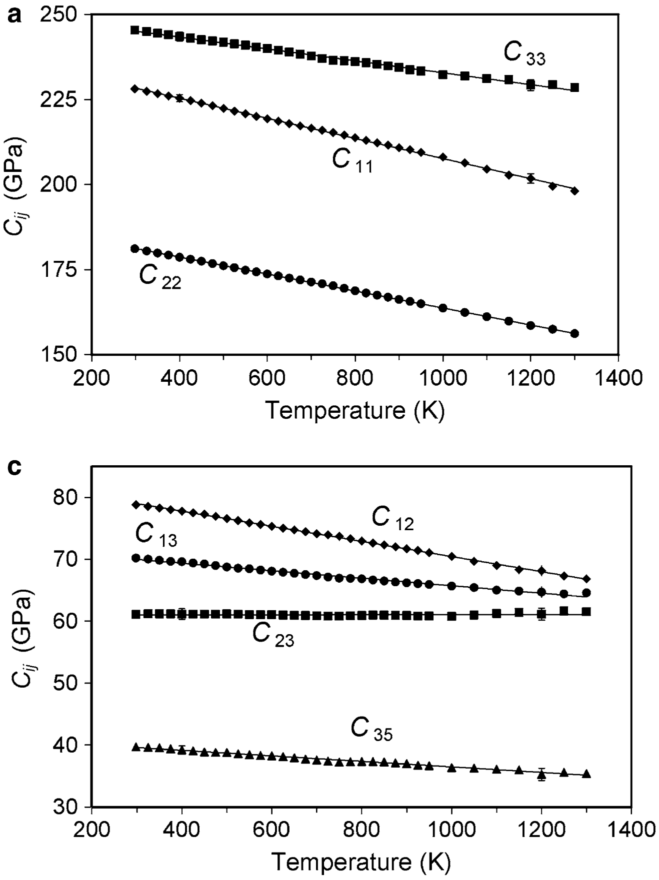

Fig. 2 **a** C_{11}, C_{22}, and C_{33} versus T; **b** C_{44}, C_{55}, and C_{66} versus T; **c** C_{12}, C_{13}, C_{23}, and C_{35} versus T; and **d** C_{15}, C_{25}, and C_{46} versus T for chrome-diopside. Representative error bars shown at 400 and 1,200 K (350 and 1,150 K for C_{46}). Uncertainties are within the symbols if error bars are not visible

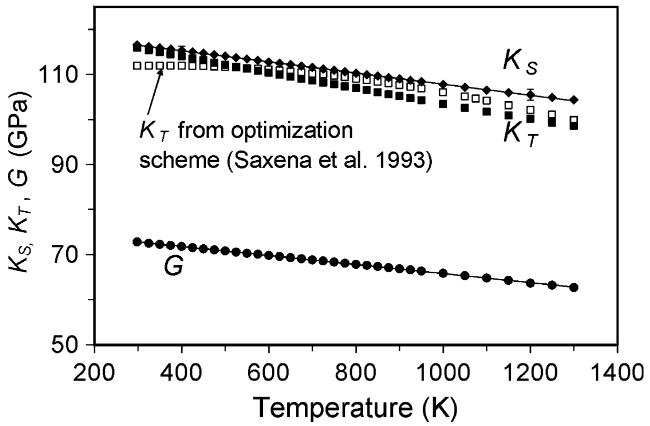

Fig. 3 The T dependences of isotropic moduli, K_S, K_T, and G, for chrome-diopside. Representative error bars shown at 400 and 1,200 K (or 1,150 K). Uncertainties are within the symbols if error bars are not visible

capacity at constant pressure C_P provided by Saxena et al. (1993) for clinodiopside (values reproduced in Table 2). The Saxena et al. (1993) tabulation provides plausible details for $\alpha(T)$ from an optimization procedure. These details are not resolvable in the direct expansivity measurements (Cameron et al. 1973; Finger and Ohashi 1976); the measurements only provide an average value of α over a range of T. The average obtained from the expansivity measurements is, however, consistent with the average $\alpha(T)$ from room T to 1,300 K in the Saxena et al. (1993) tabulation.

Figure 4 illustrates the T dependences of the isotropic compressional and shear wave velocities, V_P and V_S, respectively, obtained from K_S, G, and ρ through the well-known relations:

$$V_P = \sqrt{\frac{K_S + \frac{4}{3}G}{\rho}} \tag{3}$$

and

$$V_S = \sqrt{\frac{G}{\rho}}. \tag{4}$$

Values for the T dependences of the isotropic elastic properties and wave velocities are also given in Table 1, along with corresponding values for bronzite.

The magnitudes of T derivatives of isotropic moduli, especially K_S and K_T, and consequently V_P, are considerably less for the chrome-diopside studied here than they are for orthopyroxene (see Table 1). We find remarkable agreement with the Duffy and Anderson (1989) predictions of both $(\partial K_S/\partial T)_P$ and $(\partial G/\partial T)_P$ for clinopyroxene. Our measured values are $(\partial K_S/\partial T)_P = -0.0123$ GPa K^{-1} and $(\partial G/\partial T)_P = -0.00998$ GPa K^{-1}, compared to -0.013 GPa K^{-1} and -0.010 GPa K^{-1} predicted from systematics (Duffy and Anderson 1989). These derivatives for K_S and G are the lowest in magnitude of any of the main minerals of Earth's mantle.

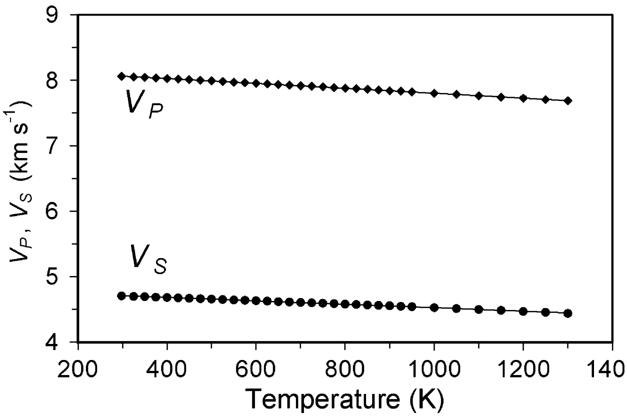

Fig. 4 The T dependences of wave speeds, V_P and V_S, for chrome-diopside. Uncertainties are within the symbols

There remain uncertainties regarding orthopyroxene T derivatives of elasticity and, therefore, the extent that elastic properties of ortho- and clinopyroxene can be used as proxies for each other. The measured value of $(\partial K_S/\partial T)_P = -0.0268$ GPa K^{-1} for bronzite (Frisillo and Barsch 1972), an orthopyroxene, compares to -0.012 GPa K^{-1} predicted by Duffy and Anderson (1989). Duffy and Anderson (1989) discounted the measured values of the first P and T derivatives of elasticity for bronzite on the grounds that these derivatives are anomalous and large negative second deriviatives will quickly bring them to normal values. It seems, however, that large negative second derivatives are pertinent to P effects, but they do not explain anomalous T derivatives. Perhaps the large magnitude of $(\partial K_S/\partial T)_P$ measured for bronzite is a precursor of mode softening occurring at higher T (Jackson et al. 2004). In any case, our confirmation of the Duffy and Anderson (1989) predictions for the clinopyroxene $(\partial K_S/\partial T)_P$ and $(\partial G/\partial T)_P$ values engenders renewed confidence in their estimates of these derivatives for orthopyroxene.

It is also uncertain to what extent differences in measured values of $(\partial K_S/\partial T)_P$, $(\partial K_T/\partial T)_P$, and $(\partial V_P/\partial T)_P$ between diopside and bronzite result from dissimilar compositions of the minerals. Of particular note is the presence of calcium in diopside. The P derivative of K_T for clinopyroxene appears sensitive to composition. Levien et al. (1979) report $(\partial K_T/\partial P)_T = 4.8 \pm 0.7$ for diopside from single-crystal data obtained on a four-circle X-ray diffractometer with a diamond cell, a value that was later revised to 4.5 ± 1.8 (Levien and Prewitt 1981). Recently, Kung et al. (2004) found $(\partial K_T/\partial P)_T = 5.5 \pm 0.3$ for clino-$\mathrm{MgSiO_3}$ at 6.5 GPa, which is significantly higher than for calcium-rich diopside, although the stated error in the diopside experimental value is large (Levien and Prewitt 1981). Similar comparisons to determine compositional effects on $(\partial K_S/\partial T)_P$ in clinopyroxene cannot be made because there are no T data on compositions other than diopside. In some systems, such as garnets, the magnitudes of $(\partial K_S/\partial T)_P$, $(\partial K_T/\partial T)_P$, and $(\partial V_P/\partial T)_P$ decrease with increasing

Table 2 Thermodynamic and thermoelastic properties of chrome-diopside from 298 to 1300 K

T (K)	α^{a} (10^{-5} K^{-1})	ρ^{b} (10^{3} kg m^{-3})	C_P^{a} (J mol^{-1} K^{-1})	γ	δ_S	δ_T	Γ	αK_T (10^{-3} GPa K^{-1})
298	1.88	3.286	83.30	0.867	5.61	8.16	7.29	2.18
350	2.41	3.282	91.18	1.009	4.41	6.43	5.74	2.77
400	2.72	3.278	97.34	1.065	3.92	5.73	5.11	3.11
450	2.94	3.273	102.28	1.089	3.65	5.35	4.77	3.33
500	3.09	3.269	106.26	1.100	3.49	5.12	4.56	3.47
550	3.21	3.263	109.50	1.104	3.38	4.97	4.42	3.58
600	3.31	3.258	112.19	1.105	3.30	4.87	4.32	3.66
650	3.39	3.253	114.45	1.105	3.24	4.79	4.25	3.71
700	3.46	3.247	116.38	1.105	3.19	4.73	4.20	3.76
750	3.52	3.241	118.06	1.104	3.15	4.69	4.15	3.80
800	3.58	3.236	119.53	1.104	3.12	4.65	4.12	3.83
850	3.63	3.230	120.84	1.104	3.09	4.62	4.09	3.85
900	3.68	3.224	122.01	1.105	3.06	4.60	4.06	3.87
950	3.73	3.218	123.08	1.105	3.04	4.58	4.04	3.89
1000	3.77	3.212	124.06	1.106	3.02	4.56	4.02	3.90
1050	3.82	3.206	124.97	1.108	3.00	4.54	4.00	3.92
1100	3.87	3.200	125.81	1.109	2.98	4.53	3.98	3.93
1150	3.91	3.193	126.61	1.111	2.97	4.52	3.97	3.94
1200	3.96	3.187	127.35	1.113	2.95	4.50	3.95	3.95
1250	4.00	3.181	128.06	1.115	2.93	4.49	3.94	3.96
1300	4.05	3.174	128.74	1.117	2.92	4.48	3.93	3.97

[a] Saxena et al. (1993); same average $\alpha(T)$ as by Cameron et al. (1973) and Finger and Ohashi (1976) from 298 to 1,300 K, but differ in some details (see the text)

[b] Calculated from $\alpha(T)$ of column 2

calcium content (Isaak et al. 1992). However, the difference in these derivatives when comparing between calcium-poor and calcium-rich garnets is not nearly as significant as is found when comparing diopside with bronzite. Further, the magnitude of $(\partial G/\partial T)_P$ increases when going from pyrope(calcium-poor garnet) to grossular (calcium-rich garnet), contrary to what is found when comparing $(\partial G/\partial T)_P$ of bronzite (calcium-poor pyroxene) with that of diopside (calcium-rich pyroxene), suggesting factors other than composition are affecting the T derviatives when comparing between pyroxene materials. Additional T data are required to understand the extent to which $(\partial K_S/\partial T)_P$ depends on structure and composition in ortho- and clinopyroxenes.

We calculated several dimensionless parameters important to geophysics from our new elasticity data (see Table 2). Figures 5 and 6 show the respective T dependences of the Grüneisen parameter γ and the quantity v defined by

$$v = \left(\frac{\partial \ln V_S}{\partial \ln V_P}\right)_P, \tag{5}$$

The display of γ in Fig. 5 compares favorably with values tabulated by Saxena et al. (1993) based on their optimization scheme. It must be emphasized, however, that while the current γ results incorporate new measured values of K_S; both sets of γ displayed in Fig. 5 were computed from the same values of α and C_P . Figure 6 shows values for v near 1.2 and virtually independent of T. These results are very similar to those found for endmember forsterite (Isaak et al. 1989) and iron-bearing olivine (Isaak 1992). Indeed, a survey of tables in Anderson and Isaak (1995) reveals that values of v for several materials are approximately independent of T and in the range of 1.10–1.30; diopside conforms to this trend.

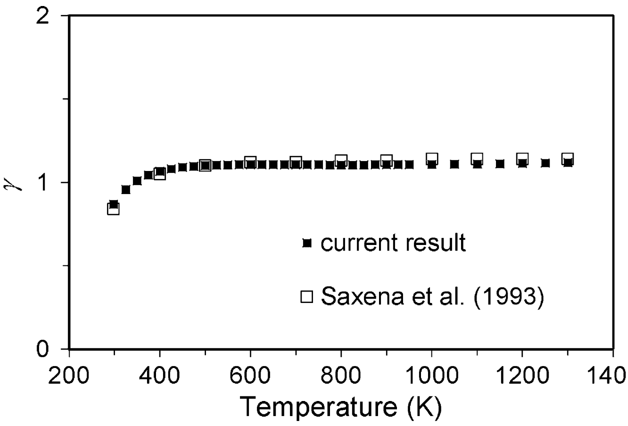

Fig. 5 The T dependence of the Grüneisen parameter γ (dimensionless) for chrome-diopside

Figure 7 illustrates the T dependences of the three dimensionless parameters, δ_S, δ_T, and Γ, defined by

$$\delta_S = -\frac{1}{\alpha K_S}\left(\frac{\partial K_S}{\partial T}\right)_P, \tag{6}$$

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P, \tag{7}$$

and

$$\Gamma = -\frac{1}{\alpha G}\left(\frac{\partial G}{\partial T}\right)_P. \tag{8}$$

The graphs show these three parameters are all approximately independent of T at high T, as is the case for many other materials, and have values that fall in the range typical for many other mantle materials

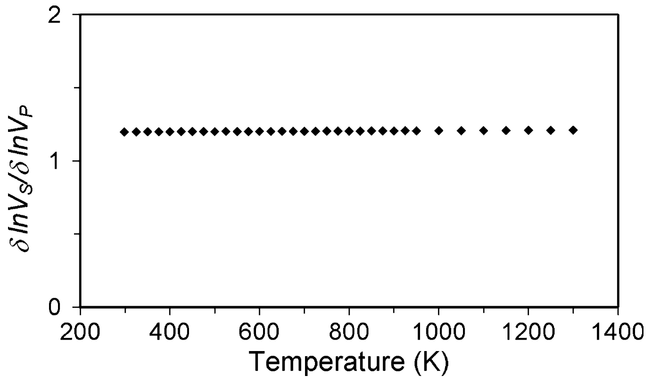

Fig. 6 The T dependence of the parameter ν (dimensionless) for chrome-diopside

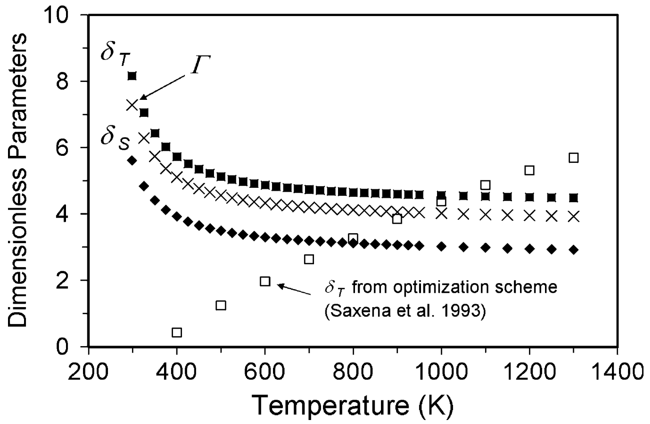

Fig. 7 The T dependences of three dimensionless parameters, δ_S, δ_T, and Γ, for chrome-diopside

(Anderson et al. 1992). We also see the approximation $\delta_T \approx \Gamma$ occasionally used in studies of Earth properties is correct to within 10% for diopside. Figure 7 also shows the δ_T listed by Saxena et al. (1993) differs significantly from our determination of this parameter. Values of $K_T(T)$ provided by Saxena et al. (1993) are close to those found in our experiments (Fig. 3). However, $\delta_T(T)$ is controlled by details in $(\partial K_T/\partial T)_P$. Our results are based on precise measurements of $(\partial K_T/\partial T)_P$.

Finally, Fig. 8 shows values of $\alpha K_T(T)$ calculated from K_T. These data reveal that $\alpha K_T(T)$ approaches a constant value at elevated T, as suggested earlier from the optimization scheme used by Saxena et al. (1993). Since

$$\left(\frac{\partial(\alpha K_T)}{\partial T}\right)_P \approx 0 \tag{9}$$

at high T, the thermal pressure P_{TH} defined by

$$\Delta P_{\mathrm{TH}} = \int_{T_\mathrm{i}}^{T_\mathrm{f}} (\alpha K_T)\,\mathrm{d}T \tag{10}$$

of diopside can be expressed as a linear function of final temperature T_f via

$$\Delta P_{\mathrm{TH}} = \alpha K_T (T_\mathrm{f} - T_\mathrm{i}) \tag{11}$$

provided T_i is at, or above, the T for which αK_T levels out (see Fig. 8). This linearized form of the thermal pressure has been widely discussed elsewhere, having been observed in several other higher symmetry minerals [see, e.g., Anderson (1999)], and is an important consideration in thermal equations of state.

Anderson (1999) also discusses the importance of the anharmonic term $[\partial(\alpha K_T)/\partial V]_T$ and reviews approximate values of this parameter for several minerals. If

$$\left[\frac{\partial(\alpha K_T)}{\partial V}\right]_T \approx 0, \tag{12}$$

then the material is said to have no anharmonicity in αK_T with respect to volume V and the equation of state for the material can be expressed in a simplified form as

$$P(V,T) = P(V,T_0) + P_{\mathrm{TH}}(V_0, \Delta T) \tag{13}$$

where V_0 refers to the uncompressed V at a reference temperature T_0 and $\Delta T = T_\mathrm{f} - T_0$. The attractive feature of (13) is that the first term on the right side is a function only of V (or P) and the second term depends only on T. It turns out that $[\partial(\alpha K_T)/\partial V]_T$ can be written in terms of its thermodynamic equivalent as

$$\left[\frac{\partial(\alpha K_T)}{\partial V}\right]_T = \frac{\alpha K_T}{V}\left[\delta_T - \left(\frac{\partial K_T}{\partial P}\right)_T\right]. \tag{14}$$

So, a test of the validity of (12), and therefore (13), is whether

$$\delta_T - \left(\frac{\partial K_T}{\partial P}\right)_T \approx 0. \tag{15}$$

The condition for no anharmonicity expressed by (12) and (15) can now be evaluated for diopside. Our results showing $\delta_T \approx 4.5$ (see Fig. 8), together with the Levien and Prewitt (1981) value for $(\partial K_T/\partial P)_T = 4.5 \pm 1.8$, indicate (12) and (15) are indeed excellent approximations, within the experimental uncertainty

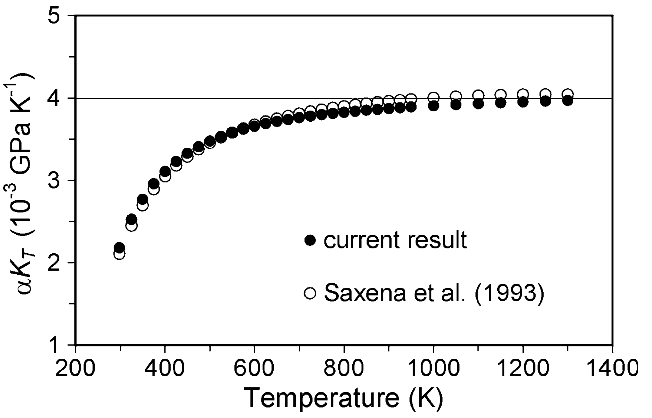

Fig. 8 The T dependence of αK_T for chrome-diopside

(which is significant for $K_T{}'$), and that the diopside equation of state can be expressed in the form given by (13).

In summary, we present data on the complete adiabatic elastic tensor for single-crystal chrome-diopside from 298 to 1,300 K. These data are the first published results for the T dependences of the 13 individual elastic constants C_{ij} of any clinopyroxene mineral. Some derivatives computed from these data, notably $(\partial K_S/\partial T)_P$, $(\partial K_T/\partial T)_P$, and $(\partial V_P/\partial T)_P$, have smaller magnitudes than all other minerals of importance in Earth's mantle, thus, confirming predictions from systematics studies (Duffy and Anderson 1989). These data allow precise determinations of several dimensionless parameters such as γ, δ_T, δ_S, Γ and ν, to be made at high temperature for a low symmetry material. We find these parameters have normal values, when comparisons are made with other mantle minerals. Further, we demonstrate that αK_T for diopside is approximately independent of both T and volume V at elevated temperature, so its equation of state is accurately expressed in simplified form, as is the case for many high-symmetry materials of importance in Earth's mantle.

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