Non-monotonic compositional dependence of isothermal bulk modulus of the $(Mg_{1−x}Mn_x)Cr_2O_4$ spinel solid solutions, and its origin and implication

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Abstract

The compressibility of the spinel solid solutions, $(Mg_{1−x}Mn_x)Cr_2O_4$ with $x = 0.00$ (0), 0.20 (0), 0.44 (2), 0.61 (2), 0.77 (2) and 1.00 (0), has been investigated by using a diamond-anvil cell coupled with synchrotron X-ray radiation up to ~10 GPa (ambient T). The second-order Birch−Murnaghan equation of state was used to fit the $P−V$ data, yielding the following values for the isothermal bulk moduli (K_T), 198.2 (36), 187.8 (87), 176.1 (32), 168.7 (52), 192.9 (61) and 199.2 (61) GPa, for the spinel solid solutions with $x = 0.00$ (0), 0.20 (0), 0.44 (2), 0.61 (2), 0.77 (2) and 1.00 (0), respectively (K'_T fixed as 4). The K_T value of the $MgCr_2O_4$ spinel is in good agreement with existing experimental determinations and theoretical calculations. The correlation between the K_T and x is not monotonic, with the K_T values similar at both ends of the binary $MgCr_2O_4−MnCr_2O_4$, but decreasing towards the middle. This non-monotonic correlation can be described by two equations, $K_T = −49.2$ (11)$x + 198.0$ (4) ($x \leq$ ~0.6) and $K_T = 92$ (41)$x + 115$ (30) ($x \geq$ ~0.6), and can be explained by the evolution of the average bond lengths of the tetrahedra and octahedra of the spinel solid solutions. Additionally, the relationship between the thermal expansion coefficient and composition is correspondingly reinterpreted, the continuous deformation of the oxygen array is demonstrated, and the evolution of the component polyhedra is discussed for this series of spinel solid solutions. Our results suggest that the correlation between the K_T and composition of a solid solution series may be complicated, and great care should be paid while estimating the K_T of some intermediate compositions from the K_T of the end-members.

1. Introduction

Isothermal bulk modulus (K_T) is an important parameter in studies of the deep interior of the Earth (e.g., Duffy and Wang, 1998). It has been intensively investigated by different techniques such as high-P compression experiment (e.g., Mao et al., 1969; Hazen, 1993; Fei and Mao, 1993; Shieh et al., 2006), ultrasonic interferometry (e.g., Liebermann et al., 1977; Li et al., 1998), Brillouin scattering (e.g., Weidner et al., 1984; Jackson et al., 2000), empirical calculation (e.g., Anderson and Nafe, 1965; Hazen and Yang, 1999), advanced theoretical simulation (Oganov et al., 2000; Deng et al., 2010), and many more. In the last century, much

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knowledge about the K_T of minerals has been obtained and enormously expanded our understanding about the geochemical and geophysical process of the deep Earth (e.g., Ricolleau et al., 2009; Liu et al., 2012).

With some notable exceptions (e.g., Mao et al., 1969; Hazen, 1993; Higo et al., 2006; Liu et al., 2011; Nestola et al., 2011a; He et al., 2012; Yamanaka et al., 2013; Huang and Chen, 2014; Du et al., 2015), numerous experimental investigations have been devoted to determining the K_T of pure end-members of minerals. Most geologically important minerals like olivine (Ol), pyroxene, garnet (Grt), spinel ("spinel" *sensu lato*; Sp), plagioclase, amphibole and mica, however, are extremely complicated solid solutions, in terms of mineral chemistry and crystal structure. Consequently, the K_T values of a series of solid solutions may vary significantly (He et al., 2012). And more importantly, they may have a complicated compositional dependence, as recently demonstrated by Du et al. (2015) for the pyrope-grossular Grt solid solutions $((Mg_{1-x}Ca_x)_3Al_2Si_3O_{12}-Grt_{ss})$. On the other hand, large amounts of direct experimental determinations on the K_T values of different compositions for one series of solid solutions are usually unavailable, and the potentially complicated compositional effect is often unquantified. As a result, the K_T values for the minerals with compositions practically relevant to the Earth have to be approximated from the measurements on the end-members by assuming a generally linear compositional dependence (e.g., Powell and Holland, 1985; Ita and Stixrude, 1992; Stixrude and Lithgow-Bertelloni, 2005). Alternatively, they may be simply assumed as compositionally independent (e.g., Cammarano et al., 2005a, 2005b). This is hardly satisfactory. When the mineral solid solutions vary their compositions, the lengths and characteristics of their chemical bonds, and the relative sizes and roles of their component polyhedra may vary significantly and in complicated ways, so that their K_T values can not be easily predicted, as demonstrated here for the Sp solid solution series (Sp$_{ss}$) along the MgCr$_2$O$_4$−Sp and MnCr$_2$O$_4$−Sp join in this study.

Chromium spinels have the general chemical formula MCr$_2$O$_4$ and the space group $Fd\overline{3}m$ (No. 227; $Z = 8$). In their structure, the oxygens form a cubic close packing array (equipoint 32e), the M cations occupy one eighth of the tetrahedral (equipoint 8a) sites and the Cr^{3+} cations occupy half of the octahedral (equipoint 16d) sites. Due to the large excess octahedral crystal field stabilization energy of Cr^{3+} (−160 kJ/mol; O'Neill and Navrotsky, 1984), significant disordering (cations M and Cr^{3+} switching their sites) is not expected. This gives us an opportunity to closely examine the influence of the compositional variation of the tetrahedral sites on the bond lengths of different chemical bonds, the volumetric systematics of different component polyhedra, and the K_T values of the MCr$_2$O$_4$−Sp. The result may deepen our understanding of the controlling factors of the K_T of other mineral solid solutions.

MgCr$_2$O$_4$−Sp plays a very important role in the partial melting process of the upper mantle (Liu and O'Neill, 2004). With the substitution of Mg by Mn on the tetrahedral sites, a large range of solid solutions may form, as implied by some field work conducted a long time ago (Graham, 1978; Paraskevopoulos and Economou, 1981). Recently we synthesized a full series of Sp solid solutions along the join MgCr$_2$O$_4$−MnCr$_2$O$_4$, abbreviated as (Mg$_{1-x}$Mn$_x$)Cr$_2$O$_4$−Sp$_{ss}$ hereafter, and directly confirmed those field observations (Wang et al., 2012). Considering the large size difference (~12%) between the Mg^{2+} (0.585 Å) and Mn^{2+} (0.655 Å) on a tetrahedral site (O'Neill and Navrotsky, 1983), this is important. Additionally, we investigated the volume-composition relationship, and determined the effect of the Mg−Mn substitution on the thermal expansivities (Wang et al., 2012).

In this study, we conducted a large number of high-P experiments to investigate the compressibility of the (Mg$_{1-x}$Mn$_x$)Cr$_2$O$_4$−Sp$_{ss}$, and found a non-monotonic compositional effect on the K_T. On the basis of the new result, we reexamined the compositional effect on the thermal expansion coefficients reported by Wang et al. (2012), and discovered a non-monotonic compositional effect as well. Furthermore, we explored the origin of this non-monotonic compositional effect by resorting to the variations of the constituent chemical bonds, the distortion evolution of the oxygen array and the mixing behaviors of the component polyhedra in the (Mg$_{1-x}$Mn$_x$)Cr$_2$O$_4$−Sp$_{ss}$, and discussed some of its implications to other mineral solid solutions pertinent to the geosciences.

2. Experiments

The (Mg$_{1-x}$Mn$_x$)Cr$_2$O$_4$−Sp$_{ss}$, with $x = 0.00$ (0), 0.20 (0), 0.44 (2), 0.61 (2), 0.77 (2) and 1.00 (0), were synthesized in an open air at 1200 °C for 48 h by using a conventional muffle furnace (Wang et al., 2012). Their compositional and powder X-ray diffraction (XRD) data suggested that they were essentially 2−3 spinels, with nearly all Mg^{2+} cations and Mn cations (appearing as Mn^{2+}) on the tetrahedral sites and nearly all Cr cations (occurring as Cr^{3+}) on the octahedral sites. This observation was fully compatible with previous studies (Raccah et al., 1966; O'Neill and Dollase, 1994; Gilewicz-Wolter et al., 2005; Stefan and Irvine, 2011). Arguably, a trace amount of Cr^{4+} or Cr vacancy might be present according to O'Neill and Dollase (1994) or Moriwake et al. (2002), respectively, but its amount is too small to be meaningful to the physical properties of the Sp$_{ss}$.

To investigate the compression behavior, we have carried out high-P powder X-ray diffraction experiments (ambient T) at the beamline X17C, National Synchrotron Light Source, Brookhaven National Laboratory. We compressed the (Mg$_{1-x}$Mn$_x$)Cr$_2$O$_4$−Sp$_{ss}$ up to ~10 GPa with a symmetrical diamond-anvil cell (DAC). Since the experimental techniques have been well established and routinely used by our group (e.g., Liu et al., 2009, 2011; Chang et al., 2013; Xiong et al., 2015), they are only briefly described here. We used T301 stainless steel plates as the gaskets, a 1:4 ethanol-methanol mixture as the pressure media, and the ruby fluorescence method as the P scale (Mao et al., 1978). The incident synchrotron X-ray beam was monochromatized to a wavelength of either 0.4066 or 0.4112 Å, and its beam size was collimated

to a size of about ~25 × 20 μm^2. The X-ray diffraction data were collected for 600–1200 s using an online CCD detector, and later processed to generate the conventional one-dimension X-ray profile using the Fit2D program (Hammersley, 1996). With a full profile refinement of the collected X-ray data, the positions of the diffraction peaks such as 111, 220, 311, 222, 400, 331, 422, 511, 440 and 531 were determined, and the unit-cell parameters of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ at different P were subsequently refined from them.

3. Results and discussions

Our high-P experiments for the $MgCr_2O_4-Sp$ were conducted up to ~10.3 GPa. According to Wang et al. (2002), Yong et al. (2012) and Nestola et al. (2014), no phase transition should be expected for this Sp_{ss} in the investigated P range, which was confirmed by the present DAC experiments. Furthermore, the high-P experiments for other $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ with x = 0.20 (0), 0.44 (2), 0.61 (2), 0.77 (2) and 1.00 (0) were carried out up to ~5.46, 10.33, 5.84, 7.56 and 9.12 GPa, respectively. No phase transition was observed in these compression experiments as well. Table 1 summarises the unit-cell parameters at different pressures derived from our X-ray diffraction patterns. In total, 42 sets of unit-cell parameters have been obtained for the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ in this study.

3.1. K_T of the $MgCr_2O_4-Sp$

Fig. 1 shows the $P-V$ data of the $MgCr_2O_4-Sp$ obtained in this study, along with the $P-V$ data from previous experimental investigations (up to 19.49 GPa by Yong et al. (2012) and up to 9.2 GPa by Nestola et al. (2014)). All data at P below ~14 GPa from these different studies appear in good agreement. Due to the somehow imperfect performance of the employed pressure medium of argon in maintaining a hydrostatic condition in the DAC experiments at high P (Klotz et al., 2009), the two data at ~14 GPa reported by Yong et al. (2012) might be subject to minor P overestimate only, but the two data at 18 and 19.49 GPa should have been significantly affected (Fig. 1). Anyhow, these four data are not particularly meaningful since the maximum stable P for the $MgCr_2O_4-Sp$ at geologically relevant T is less than ~14 GPa (Ishii et al., 2015).

The reduction of the unit-cell volume of the $MgCr_2O_4-Sp$ achieved by our DAC experiments was ~4.64% only (Table 1). Considering this relatively small volume reduction, we have chosen to fit the $P-V$ data to the second-order Birch–Murnaghan EoS (BM-EoS; Birch, 1947) by a least-squares method, in order to determine the K_T:

$$P = 3K_Tf_E(1 + 2f_E)^{\frac{5}{2}}, \qquad (1)$$

where f_E is the Eulerian definition of finite strain, $[(V_0/V)^{2/3}-1]/2$. In the Eulerian definition of the finite strain, V_0 and V are the volume at zero pressure and high pressure, respectively. The first derivative of K_T, K_T', is thus assumed as 4.

Table 1
Unit-cell parameters of $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ at different pressures (ambient T)[a].

x	P (GPa)[b]	a (Å)	V (Å^3)
0.00 (0)[c]	0.0001 (0)	8.3364 (1)	579.34 (1)
	0.50 (5)	8.3237 (6)	576.69 (12)
	1.81 (5)	8.3069 (11)	573.22 (22)
	3.24 (5)	8.2884 (7)	569.38 (14)
	4.30 (5)	8.2740 (10)	566.42 (19)
	6.23 (5)	8.2505 (4)	561.61 (8)
	7.31 (5)	8.2436 (16)	560.21 (33)
	8.39 (5)	8.2296 (9)	557.36 (18)
	9.28 (5)	8.2219 (3)	555.80 (7)
	10.32 (5)	8.2071 (10)	552.80 (21)
0.20 (0)	0.0001 (0)	8.3579 (1)	583.83 (1)
	0.74 (10)	8.3421 (6)	580.53 (11)
	1.67 (10)	8.3301 (10)	578.02 (20)
	2.59 (10)	8.3202 (9)	575.96 (18)
	4.07 (10)	8.2991 (12)	571.61 (26)
	5.46 (13)	8.2878 (13)	569.28 (28)
0.44 (2)	0.0001 (0)	8.3819 (2)	588.87 (2)
	0.71 (5)	8.3642 (6)	585.14 (12)
	2.47 (5)	8.3400 (5)	580.09 (10)
	3.79 (5)	8.3204 (6)	576.00 (11)
	4.57 (9)	8.3115 (8)	574.16 (15)
	5.30 (5)	8.3002 (8)	571.83 (15)
	6.35 (6)	8.2877 (9)	569.25 (17)
	7.35 (5)	8.2783 (6)	567.32 (11)
	8.14 (10)	8.2690 (10)	565.40 (21)
	9.14 (12)	8.2557 (11)	562.69 (24)
	10.33 (9)	8.2367 (15)	558.80 (32)
0.61 (2)	0.0001 (0)	8.4062 (2)	593.68 (2)
	0.40 (5)	8.3974 (8)	592.15 (16)
	1.40 (5)	8.3758 (9)	587.60 (19)
	2.53 (5)	8.3613 (12)	584.56 (26)
	3.61 (9)	8.3471 (7)	581.56 (15)
	4.66 (6)	8.3331 (7)	578.65 (14)
	5.84 (15)	8.3196 (7)	575.84 (14)
0.77 (2)	0.0001 (0)	8.4214 (1)	597.24 (1)
	1.00 (26)	8.4124 (7)	595.32 (14)
	2.12 (10)	8.3865 (9)	589.84 (19)
	3.18 (10)	8.3679 (10)	585.95 (21)
	4.10 (10)	8.3627 (12)	584.84 (26)
	5.46 (10)	8.3466 (9)	581.46 (19)
	6.38 (10)	8.3361 (10)	579.28 (20)
	7.56 (10)	8.3265 (12)	577.29 (26)
1.00 (0)	0.0001 (0)	8.4393 (1)	601.07 (1)
	1.62 (10)	8.4277 (15)	598.59 (32)
	2.50 (10)	8.4138 (13)	595.64 (29)
	3.60 (10)	8.3947 (9)	591.57 (18)
	6.90 (10)	8.3414 (15)	580.38 (33)
	9.12 (11)	8.3217 (13)	576.28 (29)

[a] Data at ambient P and T are from Wang et al. (2012).
[b] P in the high-P experiments was determined by averaging the values measured before and after collection of synchrotron data. Fully hydrostatic pressure was potentially not maintained in the experiments, so that a P error of 0.05 GPa was assumed for samples of x = 0.00, 0.41 and 0.61 wherever the measured P error was less than 0.05 GPa, and a P error of 0.1 GPa was assumed for samples of x = 0.22, 0.77 and 1.00 wherever the measured P error was less than 0.1 GPa.
[c] Number in the parentheses represents one standard deviation in the rightmost digit.

The assumption of $K_T' = 4$ for the $MgCr_2O_4-Sp$ is sound. The K_T' value was experimentally determined as either 7.2 (3) (Yong et al., 2012) or 5.8 (4) (Nestola et al., 2014), with the former generally influenced by the non-hydrostatic condition in
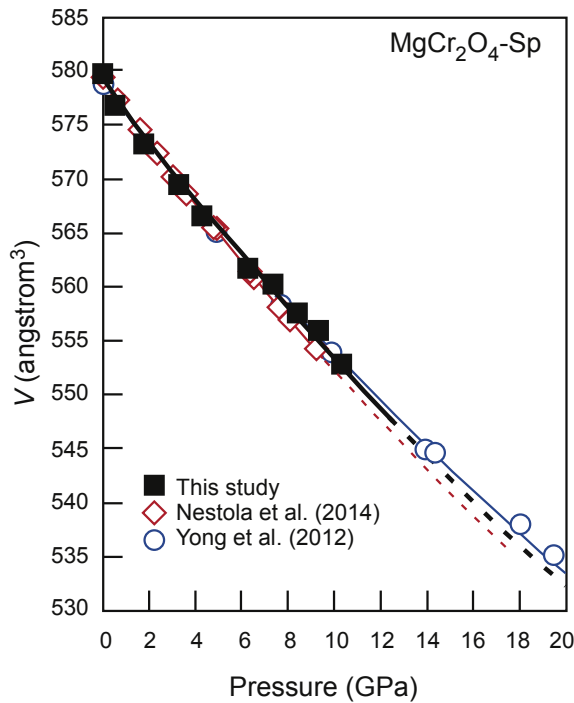
Fig. 1. $V−P$ relations for the $MgCr_2O_4−Sp$ from different experimental studies (ambient T). Curves are drawn according to the regressed BM-EoS parameters, as listed in Table 2 (with K'_T set at 4). For most data, their error bars are equal to or smaller than the symbols.

similar K'_T values, 4.41 (6) (the exchange−correlation interaction treated with the generalized gradient approximation; GGA) and 4.5 (1) (the exchange−correlation interaction treated with the local density approximation; LDA). It is thus clear that the K'_T values for the $MgCr_2O_4−Sp$ must be close to 4.

Using our $P−V$ data for the $MgCr_2O_4−Sp$ (Table 1) and with the assumption of $K'_T = 4$, we have obtained the following BM-EoS parameters: $V_0 = 579.33$ (4) $\mathring{A}^3$ and $K_T = 198.2$ (36) GPa. If we assumed $K'_T = 4.45$, a value averaged from the results reported by Zhang et al. (2016), we would have obtained essentially identical values for the BM-EoS parameters: $V_0 = 579.33$ (4) $\mathring{A}^3$ and $K_T = 196.5$ (35) GPa. As shown in Table 2, the K_T value determined in this study is in good agreement with Yong et al. (2012; 207 (2) GPa) and Nestola et al. (2014; 189.6 (7) GPa); compared on the basis of $K'_T = 4$, it is ~4.3% lower than that from Yong et al. (2012) but ~4.5% higher than that from Nestola et al. (2014). This result is well reflected in the comparison of the $P−V$ trends from these different studies, as shown in Fig. 1.

The K_T value determined here, 198.2 (36) GPa, is very much compatible with the results from all available theoretical investigations. Previously, Catti et al. (1999) and Ottonello et al. (2007) constrained its values as 197.3 and 192.56 GPa, respectively (Table 2). Recently, Zhang et al. (2016) predicted that its value should be between 181.4 (48) GPa (GGA; low boundary) and 216.1 (11) GPa (LDA; high boundary).

3.2. Non-monotonic correlation between K_T and x of the $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$

The $P−V$ data obtained for all other $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$ are compared to those for the $MgCr_2O_4−Sp$ in Fig. 2, and are similarly processed with equation (1), with the derived EoS parameters listed in Table 2.

The variation of the K_T values with the compositions of the $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$ is illustrated in Fig. 3. As the

the DAC experiments whereas the latter inadequately accurately determined by the limited volume reduction in the high-P experiments (~4.33%, similar to what we achieved in this study). In contrast, early theoretical simulations with variant methods constrained the K'_T value as 3.94 (Catti et al., 1999) or 4.066 (Ottonello et al., 2007). Furthermore, recent first-principles calculations with the CASTEP code using density functional theory and planewave pseudopotential technique, carried out up to 19 GPa by Zhang et al. (2016), generated

Table 2
EoS parameters of $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$ at ambient P and T.

x	K_T (GPa)	K'_T [a]	V_0 ($\mathring{A}^3$)	Experimental details[b]	Data source[c]
0.00 (0)[d]	207 (2)	4	578.66 (8)	0−19.49; Ar; Gold; Powder	Yong et al. (2012)
0.00 (0)	189 (2)	7.2 (3)	578.68 (4)	0−19.49; Ar; Gold; Powder	Yong et al. (2012)
0.00 (0)	189.6 (7)	4	579.16 (5)	0−9.20; EM; Quartz; SC	Nestola et al. (2014)
0.00 (0)	182.5 (14)	5.8 (4)	579.30 (4)	0−9.20; EM; Quartz; SC	Nestola et al. (2014)
0.00 (0)	198.2 (36)	4	579.33 (4)	0−10.32; EM; Ruby; Powder	This study
0.20 (0)	187.8 (87)	4	583.83 (2)	0−5.46; EM; Ruby; Powder	This study
0.44 (2)	176.1 (32)	4	588.85 (7)	0−10.33; EM; Ruby; Powder	This study
0.61 (2)	168.7 (52)	4	593.67 (5)	0−5.84; EM; Ruby; Powder	This study
0.77 (2)	192.9 (61)	4	597.24 (3)	0−7.56; EM; Ruby; Powder	This study
1.00 (0)	199.2 (106)	4	601.07 (4)	0−9.12; EM; Ruby; Powder	This study

[a] Where the K'_T value is not 4, it has been constrained by the $P−V$ data; otherwise, it has been fixed as 4.
[b] All compression experiments were done with the DAC, with some of the experimental details listed in the following order: P range (GPa); P medium; P scale; XRD method. Ar, pressure medium of argon; EM, pressure medium of an 1:4 ethanol-methanol mixture; Gold, pressure scale of gold (Fei et al., 2007); Quartz, pressure scale of quartz (Angel et al., 1997); Ruby, pressure scale of ruby (Mao et al., 1978); Powder, powder XRD; SC, single crystal XRD.
[c] All samples were synthesized at 1 atm, and either at 1200 °C (Nestola et al., 2014; This study) or 1300 °C (Yong et al., 2012).
[d] Number in parentheses represents one standard deviation to the rightmost digit.
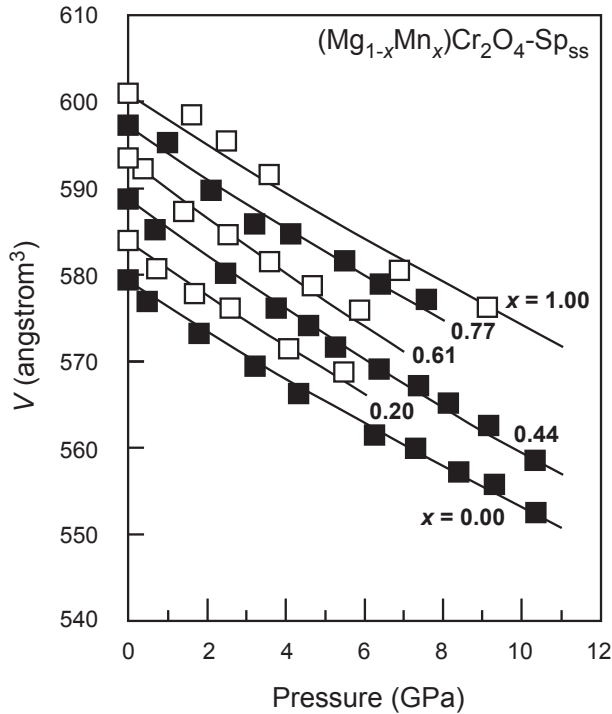
Fig. 2. $V-P$ relations for the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ observed in this study (ambient T). Curves are drawn according to the regressed BM-EoS parameters, as listed in Table 2 (with K'_T set at 4). For most data, their error bars are equal to or smaller than the symbols.
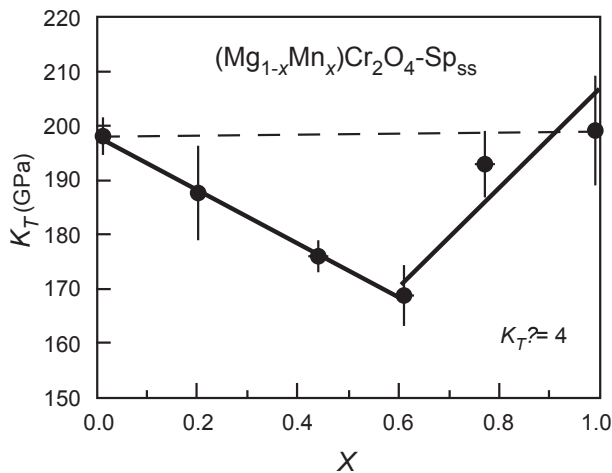

Fig. 3. Correlations between the K_T and x of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ (ambient P and T). Data at $x = 0$ and 1 are slightly shifted horizontally to display them more clearly. The broken line was drawn according to equations (5) and (6) in Stixrude and Lithgow-Bertelloni (2005), with the data for the two end-members from this study.

substitution of Mn for Mg progresses, the K_T value first decreases and late increases, with a minimum value of ~168.7 (52) approximately at $x = 0.61$. This non-monotonic correlation can be arithmetically described by the following two equations (determined with a weighted linear-squares method):

$$K_T = -49.2(11)x + 198.0(4) \quad (x \leq 0.61), \tag{2}$$

and

$$K_T = 92(41)x + 115(30) \quad (x \geq 0.61). \tag{3}$$

Evidently in Fig. 3, our K_T values for the intermediate compositions between the two end-members $MgCr_2O_4-Sp$ and $MnCr_2O_4-Sp$ are significantly different to those estimated with the assumption of an almost linear compositional dependence (Stixrude and Lithgow-Bertelloni, 2005).

The assumption of a constant K'_T value of 4 for the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ may be arguable and might affect our major findings here (equations (2) and (3)). It should be recognized that this assumption could not be critically evaluated by our experimental data due to the limited volume reductions achieved in this study. Existent investigations on other series of Sp_{ss} with identical experimental techniques, however, have suggested nearly constant K'_T values. Just to mention a few examples, the K'_T values of the $MgCr_2O_4-Sp$ and $FeCr_2O_4-Sp$ are almost identical (5.8 (4) and 6.1 (5), respectively; Nestola et al., 2014), those of the $MgAl_2O_4-Sp$ with different degrees of cation order are generally the same (5.6 (3) and 5.4 (3); Nestola et al., 2007), and those of the $(Mg_{1-x}Fe_x)_2SiO_4-Sp_{ss}$ (ringwoodites) are essentially constant (4.4 (2) for the investigated composition range $x \leq 0.5$; Higo et al., 2006). In contrast, the K'_T values for one certain Sp_{ss} determined in different experimental investigations can be very different, for example 7.2 (3) by Yong et al. (2012) and 5.8 (4) by Nestola et al. (2014) for the $MgCr_2O_4-Sp$, which was mostly caused by different experimental techniques (pressure media, pressure scales, pressure ranges, etc.) and different sample qualities.

Nevertheless, available theoretical investigation conducted with identical techniques simultaneously on both the $MgCr_2O_4-Sp$ and the $MnCr_2O_4-Sp$ indeed suggested some small fluctuation in the K'_T values, from 3.94 for the $MgCr_2O_4-Sp$ to 3.67 for the $MnCr_2O_4-Sp$ (Catti et al., 1999; Quantum-mechanical calculations conducted with the periodic unrestricted Hartree-Fock approach). According to Liu et al. (2016), this level of fluctuation may lead to an uncertainty of <5 GPa in the K_T, and is therefore unimportant. Consequently, it has to be concluded that the non-monotonic correlation between the K_T values and the compositions of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$, with the K_T values decreasing by ~30 GPa from the two end-members (198.2 (36) GPa for the $MgCr_2O_4-Sp$ and 199.2 (61) GPa for the $MnCr_2O_4-Sp$) towards the intermediate compositions (168.7 (52) GPa for the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp$ with $x = 0.61$ (2) for example), must be real.

3.3. Origin of the non-monotonic correlation between K_T and x of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$

The isothermal bulk moduli of a group of pure compounds (or end-members for complex solid solutions) with the same crystal structure are strongly dependent on their volumes (Anderson and Nafe, 1965). As proposed by Anderson and

Anderson (1970), a relationship of $K_T V_0$ = constant holds for the end-members of the Sp group, which implies a monotonic correlation between the K_T and V_0. For a series of solid solutions such as the $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$ along a binary system, the intermediate structures should be more or less strained, so that they do not necessarily follow the same pattern as the end-members do, which is clearly demonstrated here by the non-monotonic correlation between the K_T and x of the $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$ (Fig. 3). Recently, similar phenomenon was observed for the $(Mg_{1−x}Ca_x)_3Al_2Si_3O_{12}−Grt_{ss}$, which show a "W"-shaped compositional dependence of their K_T and thermal expansion coefficient (α_0) at ambient $P−T$ conditions (Du et al., 2015). Note that in both cases the compositional parameter x exerts a monotonic effect on the V_0 (Wang et al., 2012; Du et al., 2015).

For the $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$, their $V_0−x$ data at ambient P and T showed some deviation from the Vegard's law (i.e., ideal mixing; Wang et al., 2012). Here we have further explored their excess mixing volumes ($V_{0-excess}$) in Fig. 4. With the two end-members attaining zero $V_{0-excess}$ by definition (hence zero microstrain), the $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$ have a third nearly-zero $V_{0-excess}$ point locating approximately at $x = 0.5$. Additionally, two local $V_{0-excess}$ maximum points appear at about $x = 0.25$ and $x = 0.75$, which could have been better constrained with more data. Similar $V_{0-excess}$-x relationship was also observed for the $Co(Al_{1−x}Ga_x)_2O_4−Sp_{ss}$, with three zero $V_{0-excess}$ points but one $V_{0-excess}$ maximum point and one $V_{0-excess}$ minimum point (Lilova et al., 2010). It follows that the binary Sp_{ss}, with cation substitution either on the tetrahedral sites or on the octahedral sites, may have a rather complicated mixing behavior.

Both the $MgCr_2O_4−Sp$ and the $MnCr_2O_4−Sp$ are 2−3 normal spinel, and the Mg and Mn cations replace each other on the tetrahedral sites of the $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$. The size difference between the Mg^{2+} and Mn^{2+} in their fourfold coordination is large, ~12% (O'Neill and Navrotsky, 1983), so that a regular positive mixing behavior may be expected. This would have been broadly confirmed by our observation if we ignored the intermediate part of the $V_{0-excess}$-x curve (Fig. 4). Since the Sp_{ss} at about $x = 0.5$ has a nearly-zero $V_{0-excess}$, its structure should be generally microstrain-free, which presumably implies an even and ordered Mg−Mn distribution on the tetrahedral sites. It follows that this Sp_{ss} at about $x = 0.5$ may behave like a "ghost" end-member for the $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$.

The Sp structure is completely determined by its two independent cation-anion distances, termed as d_{T-O} (averaged bond length of the tetrahedron) and d_{M-O} (averaged bond length of the octahedron) in this study (Hill et al., 1979; O'Neill and Navrotsky, 1983). According to Lenaz et al. (2004) who investigated the $(Mg_{1−x}Fe_x)Cr_2O_4−Sp_{ss}$ with single-crystal X-ray diffraction method, it is appropriate to assume that the d_{T-O} varies linearly with the x for the $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$, $d_{T-O} = 1.965 + 0.07x$ Å; the radius for the Mg^{2+}, Mn^{2+} and $O^{2−}$ is 0.585, 0.655 and 1.38 Å, respectively (O'Neill and Navrotsky, 1983; Shannon, 1976). The response of the d_{M-O} to this Mg−Mn substitution can then be calculated with the following equations (Hazen and Yang, 1999),
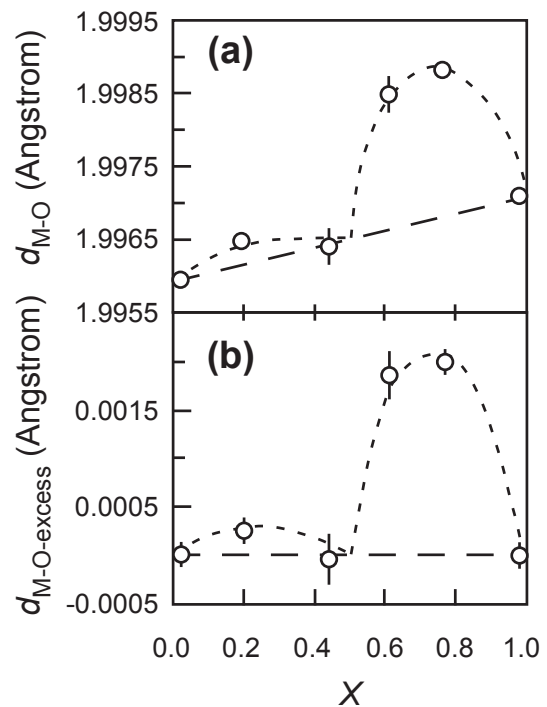

Fig. 4. Relationship between the V_0-excess and x of the $(Mg_{1−x}Mn_x)$ $Cr_2O_4−Sp_{ss}$ (ambient P and T). Data at $x = 0$ and 1 are slightly shifted horizontally to display them more clearly. The broken line was drawn for the case of an ideal mixing whereas the dash line was eye-fitted according to our calculated results.

Fig. 5. Correlations between the d_{M-O} and x (a), and between the $d_{M-O-excess}$ and x (b) of the $(Mg_{1−x}Mn_x)Cr_2O_4−Sp_{ss}$ (ambient P and T). Data at $x = 0$ and 1 are slightly shifted horizontally to display them more clearly. The broken lines represent the case of an ideal mixing whereas the dash lines were eye-fitted according to our calculated results.

$$d_{M-O} = \sqrt{\frac{A + 8d_{T-O}^2}{33}}, \qquad (4)$$

where

$$A = \left(\frac{11\sqrt{3}a - 40d_{T-O}}{8}\right)^2. \qquad (5)$$

The result is shown in Fig. 5. As the substitution of Mg by Mn progresses, the d_{M-O} firstly increases gradually up to about $x = 0.25$, secondly remains generally constant for the x interval of ~0.25–0.5, then increases quickly up to about $x = 0.75$, and finally decreases gradually towards $x = 1$. In contrast, the d_{M-O} of the $(Mg_{1-x}Fe_x)Cr_2O_4-Sp_{ss}$ remains nearly constant (Lenaz et al., 2004), presumably mainly because the size difference of the Mg^{2+} and Fe^{2+} cations is much smaller (0.585 versus 0.615 Å, or ~5.1% only; O'Neill and Navrotsky, 1983).

This complicated variation pattern of the d_{M-O}, combined with the assumed linear relationship between the d_{T-O} and x, can at least qualitatively explain the non-monotonic correlation between the K_T and x of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ (Fig. 3). For the composition interval from $x = 0$ to about $x = 0.75$, both the d_{M-O} and d_{T-O} generally increase, and the M-O and T-O bonds become weaker and hence more compressible, leading to smaller K_T values for the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ with $x = 0.20(2)$, 0.44(2) and 0.61 (2) (Table 2). For the composition interval from about $x = 0.75$ to $x = 1$, however, the d_{M-O} generally decreases whereas the d_{T-O} continuously increases, suggesting stronger M-O bonds but weaker T-O bonds. Since the number of the M-O bonds is three times that of the T-O bonds in the Sp structure, the role of the M-O bonds dominates the composition range from about $x = 0.75$ to $x = 1$, and results in increasing K_T values for the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ with $x = 0.77$ (2) and 1.00 (0) (Table 2). To quantitatively finalize all the details, more measurements on the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ with different compositions are deemed necessary.

Following the same reasoning, the combined effect of the linear correlation between the d_{T-O} and x and the constant d_{M-O} suggested by Lenaz et al. (2004) for the $(Mg_{1-x}Fe_x)Cr_2O_4-Sp_{ss}$ may result in a nearly linear relationship between the K_T and x, with a slope which may be too small for any high-P experimental investigations. Indeed, Nestola et al. (2014) investigated the $MgCr_2O_4-Sp$ and $FeCr_2O_4-Sp$ with identical experimental techniques, and reached similar K_T values (182.5 (14) GPa with $K_T' = 5.8$ (4) and 184.8 (17) GPa with $K_T' = 6.1$ (5), respectively). The intermediate compositions of the $(Mg_{1-x}Fe_x)Cr_2O_4-Sp_{ss}$ should have similar K_T as well.

3.4. Thermal expansivities of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$: a reinterpretation

The thermal expansivity of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ was experimentally investigated by Wang et al. (2012) at room P and up to 1000 °C, and a linear correlation between the α_0
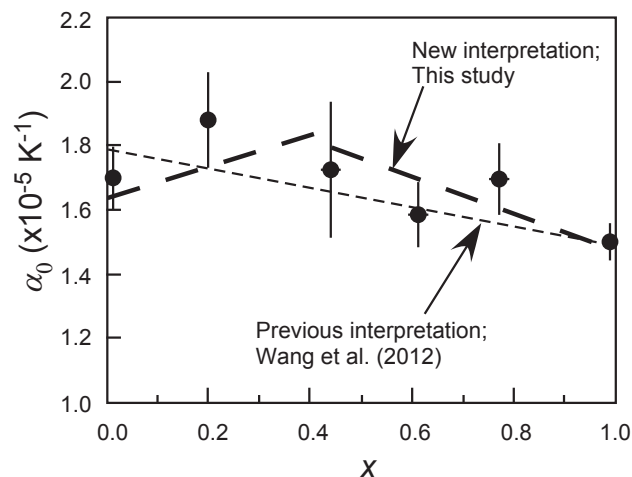

Fig. 6. Correlations between the α_0 and x of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ (ambient P and T). Data at $x = 0$ and 1 are slightly shifted horizontally to display them more clearly. Data source: Wang et al. (2012).

and x at ambient P and T was suggested (Fig. 6). In light of the non-monotonic correlation between the K_T and x observed in this study, this linear relationship needs a new interpretation. Due to the relatively small volume variations observed in Wang et al. (2012; up to ~2.40% only), the thermal expansion coefficients should have been less well constrained than the K_T. Note that the volume variations accomplished in this study were much larger, ~5.11% (Table 1).

In general, a compound easy to be compressed at high P should be ready to expand at high T, which roots in the toughness of the constituent chemical bonds. Consequently, the correlation between the α_0 and x is expected to be approximately opposite to that of the K_T and x for one certain series of solid solutions. A careful rescrutinizing of the experimental result of Wang et al. (2012) indeed suggests a possible kink for the α_0-x curve, somehow at about $x = 0.44$ rather than at $x = 0.61$ (for the K_T case), with a small increase for the approximately first half of the compositional range but a small decrease for the second half (Fig. 6). A different kink position at about $x = 0.44$ may partially reflect the relatively low accuracy of the α_0, and partially indicate the necessity of more experimental measurements. Alternatively, the difference of the kink positions may simply be real. The thermal expansivity probes the anharmonicity of the interatomic potential whereas the compressibility probes the entire potential in the region where repulsion begins to dominate, so that the K_T-x curve and the α_0-x curve for a series of solid solutions need not be exactly opposite to each other (Navrotsky, 1994). For instance, the order of the K_T and α_0 of the isochemical minerals kyanite, andalusite and sillimanite are kyanite > sillimanite > andalusite and andalusite > kyanite > sillimanite, respectively, indicating not exactly opposite roles of T and P on mineral structures (Hu et al., 2011).

Similarly, He et al. (2011, 2012) observed a generally opposite relationship between the α_0-x curve and the K_T-x

curve for the solid solutions between the lead fluorapatite and lead fluorvanadate apatite (Pb_{10} [$(PO_4)_{1-x}$ $(VO_4)_x$]$_6F_2$−Ap_{ss}): as x increases from zero to one, the α_0 linearly increases by ~13.4% whereas the K_T linearly decreases by ~16.4%. Furthermore, Tribaudino et al. (2008) and Nestola et al. (2008) observed a generally opposite relationship between the α_0-x curve and the K_T-x curve for the solid solutions between the jadeite and hedenbergite (($Na_{1-x}Al_{1-x}$)(Ca_xFe_x)Si_2O_6): as x increases from zero to one, the α_0 monotonically increases by ~15% whereas the K_T monotonically decreases by ~23.1%. In contrast, Du et al. (2015) observed subparallel, rather than opposite, "W"-shaped α_0-x curve and K_T-x curve for the ($Mg_{1-x}Ca_x$)$_3Al_2Si_3O_{12}$−Grt_{ss}. More investigation on the ($Mg_{1-x}Ca_x$)$_3Al_2Si_3O_{12}$−Grt_{ss} seems favorable.

3.5. Variations of u parameters and component polyhedra of the ($Mg_{1-x}Mn_x$)Cr_2O_4−Sp_{ss}

The primary feature of the Sp structure is a cubic close packing array of the oxygens. The positions of the oxygens are determined by the oxygen parameter u, which reflects the adjustment of the Sp structure to different cation substitutions on the tetrahedral and octahedral sites (Hill et al., 1979). The u parameter can be calculated with the following equation:

Fig. 7. Correlations between the u and x (a), and between the $u_{-excess}$ and x (b) for the ($Mg_{1-x}Mn_x$)Cr_2O_4−Sp_{ss} (ambient P and T). Data at $x = 0$ and 1 are slightly shifted horizontally to display them more clearly. The broken line in (a) and (b) represents an ideal evolution of the u and $u_{-excess}$, respectively. The dash line in (b) was eye-fitted according to our calculated results.

$$u = \frac{R^2/4 - 2/3 + (11R^2/48 - 1/18)^{1/2}}{2R^2 - 2}, \tag{6}$$

where R is the ratio of d_{M-O}/d_{T-O}; it attains the value of 0.25 for an ideal cubic close packing oxygen array. For the ($Mg_{1-x}Mn_x$)Cr_2O_4−Sp_{ss}, the calculated u gradually increases from ~0.2611 to 0.2642 as the substitution of Mg by Mn proceeds (Fig. 7a), suggesting that the oxygens move farther away from the nearest tetrahedral Mg^{2+} (or Mn^{2+}) along the [111] direction and their close packing arrangement is more distorted. In detail, however, this distortion is not strictly proportional to the magnitude of the Mg−Mn substitution, but shows some retardance to the compositional change, as indicated by the generally negative $u_{-excess}$ values in Fig. 7b. The $u_{-excess}$-x curve is evidently divided into two parts by the ($Mg_{1-x}Mn_x$)Cr_2O_4−Sp_{ss} with approximately $x = 0.5$, or the "ghost" end-member, which shows a nearly zero $u_{-excess}$ value and has a relatively relaxed structure. The negativity of the $u_{-excess}$-x curve for the ($Mg_{1-x}Mn_x$)Cr_2O_4−Sp_{ss} with $x < 0.5$ is small, implying a small capability accommodating the structural deformation caused by the Mg−Mn substitution. In comparison, the negativity of the $u_{-excess}$-x curve for the ($Mg_{1-x}Mn_x$)Cr_2O_4−Sp_{ss} with $x > 0.5$ is much larger, suggesting that large structural deformation caused by the Mg−Mn substitution can be readily absorbed. This contrast is understandable because a larger cation (Mn^{2+}) is more difficult to replace a smaller cation (Mg^{2+}) on sites dominated by the smaller cation ($x < 0.5$) than a smaller cation (Mg^{2+}) to replace a larger cation (Mn^{2+}) on sites dominated by the larger cation ($x > 0.5$).

The polyhedra in the Sp structure extensively share their edges in three dimensions, but have very different physical properties (K_T for example; Hazen and Yang, 1999; Zhang et al., 2016), so that they may have extensive but nonuniform responses to the compositional variation along a binary Sp_{ss}. Following Gracia et al. (2002), Zhang et al. (2016) fully decomposed the entire unit cell of the $MgCr_2O_4$−Sp into five types of polyhedra without introducing any volumetric overlapping, MgO_4, $(O_4)_1$, $(O_4)_2$, CrO_6 and O_6 with multiplicities 8, 8, 48, 16 and 16, respectively. They further calculated the volumes of these component polyhedra using the following equations (Yamanaka and Takéuchi, 1983):

$$V_{MgO_4} = 64V \cdot |u_{18}|^3/3, \tag{7}$$

$$V_{(O_4)_1} = 64V \cdot |u_{38}|^3/3, \tag{8}$$

$$V_{(O_4)_2} = 8V \cdot |u_{18}| \cdot |u_{38}|/3, \tag{9}$$

$$V_{CrO_6} = 128V \cdot u \cdot u_{38}^2/3, \tag{10}$$

and

$$V_{O_6} - 128V \cdot u_{18}^2 \cdot |u_{12}|/3, \tag{11}$$

where

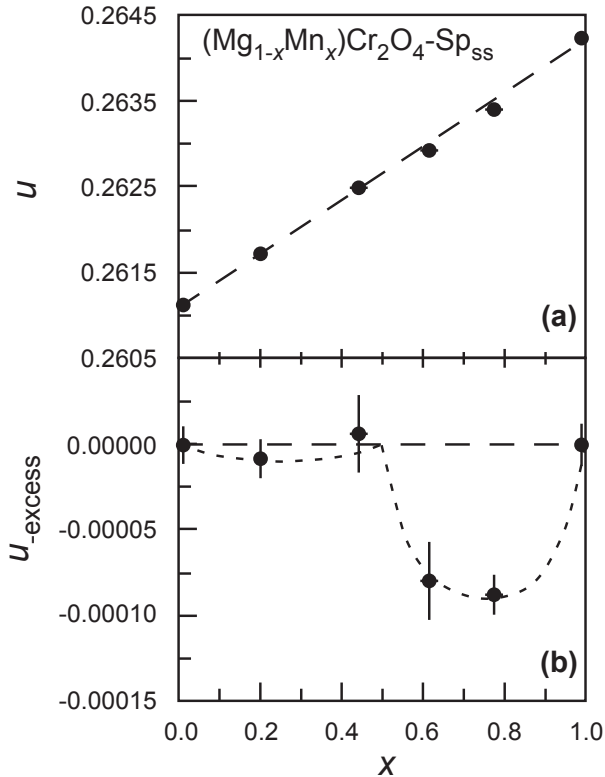$$u_{ij} = u - i/j. \tag{12}$$

Similarly, we have carried out the calculations for the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$. The results show that the volume percentages for the five types of polyhedra MgO_4, $(O_4)_1$, $(O_4)_2$, CrO_6 and O_6 in the $MgCr_2O_4-Sp$ structure are ~5.4, 3.2, 24.8, 28.9 and 37.8%, respectively. As the Mg–Mn substitution proceeds and accomplishes, the volume changes of these five types of polyhedra in the unit cells of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ are not uniform indeed: the volume of the $(Mg,Mn)O_4$ increases by ~7.1% (from 31.15 to 34.60 Å^3), that of the $(O_4)_1$ decreases by ~8.0% (from 18.27 to 17.43 Å^3), that of the $(O_4)_2$ remains almost constant (reduced by ~0.5%; from 143.70 to 148.32 Å^3), that of the CrO_6 decreases by ~4.3% (from 167.48 to 166.32 Å^3), and that of the O_6 increases by ~3.3% (from 218.74 to 234.39 Å^3). On the other hand, the total volume of the tetrahedra MgO_4, $(O_4)_1$ and $(O_4)_2$ increases by 3.75% (from 193.11 to 200.36 Å^3), and so does the total volume of the octahedra CrO_6 and O_6 (by 3.75% from 386.23 to 400.71 Å^3). A constant volume ratio of 1:2, as embedded in equations (7)–(11), is therefore maintained between these tetrahedra and these octahedra whatever the deformation extent of the oxygen array is (Fig. 7).

The volumes of the individual polyhedra (V_{-poly}) must have different responses to the compositional change as well. The V_{-poly}-x relationships are shown in Fig. 8a–e, and the $V_{-poly-excess}$-x relationships are shown in Fig. 8a*–e*.

Although volumetrically unimportant, the $(Mg,Mn)O_4$ tetrahedron shows the largest volume variation, ~11.1% (from 3.894 (4) to 4.325 (4) Å^3), as x increases from zero to one (Fig. 8a). This is totally expected since the compositional variation of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ takes place on the $(Mg,Mn)O_4$ tetrahedra. In addition, a negative $V_{-poly-excess}$-x relationship is demonstrated by our results (Fig. 8a*), as dictated by the assumed ideal mixing behavior.

In contrast, the other two types of tetrahedra, $(O_4)_1$ and $(O_4)_2$, show completely different behaviors; their V_{-poly}-x relationships and $V_{-poly-excess}$-x relationships are rather complicated (Fig. 8b and c, and Fig. 8b* and c*, respectively). Although their volumes either linearly decrease (by ~4.6% from 2.283 (3) to 2.179 (3) Å^3 for the $(O_4)_1$) or increase (by ~3.2% from 2.994 (0) to 3.090 (0) Å^3 for the $(O_4)_2$), both types of tetrahedra show generally positive mixing behaviors. In detail, their $V_{-poly-excess}$-x curves are divided into two parts approximately by the "ghost" end-member, the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ with $x = 0.5$. Interestingly, the first local maximum positivity is much smaller than the second in both cases, suggesting that the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ in the compositional range of $0.5 < x < 1$ have much larger compliances to any local strains caused by the Mg–Mn substitution.

The CrO_6 octahedron shows a peculiar volumetric variation (Fig. 8d). Its overall variation is an extremely small reduction (~0.7% from 10.468 (6) to 10.395 (6) Å^3), which is mostly expected due to its relatively large bulk modulus (~230 (30) GPa; Hazen and Finger, 1979). Against this general trend, and interestingly, the volumes of the CrO_6 octahedron in the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ at $x = 0.61$ (2) and 0.77 (2) are somehow larger than the volume of the CrO_6 octahedron in the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ at $x = 0.44$ (2). Combined with the general positive correlation between the d_{M-O} and x (Fig. 5a), the overall negative relationship between the CrO_6 volume and x implies continuous deformation of the CrO_6 octahedron. Furthermore, the $V_{-poly-excess}$-x curve is much similar to the $d_{M-O-excess}$-x curve (Figs. 8d* and 5a). Like in the cases of the $(O_4)_1$ and $(O_4)_2$ (Fig. 8b* and c*), the positive $V_{-poly-excess}$-x curve for the CrO_6 octahedron is divided into two parts by the "ghost" end-member, with the second part much more prominent than the first part.

The volume of the individual O_6 octahedron of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ increases significantly, by ~7.2% (from 13.671 (6) to 14.650 (7) Å^3; Fig. 8e). The O_6 octahedron is the second most compressible polyhedra in the $MgCr_2O_4-Sp$ (only less compressible than the MgO_4 tetrahedron; Zhang et al., 2016), and its volumetric variation comes as the second largest. The $V_{-poly-excess}$-x curve is very interesting, with the first part at $x < 0.5$ negligible whereas the second part at $x > 0.5$ distinctively positive (Fig. 8e*).

In summary, a range of structural adjustments takes place when Mn substitutes for Mg in the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$.
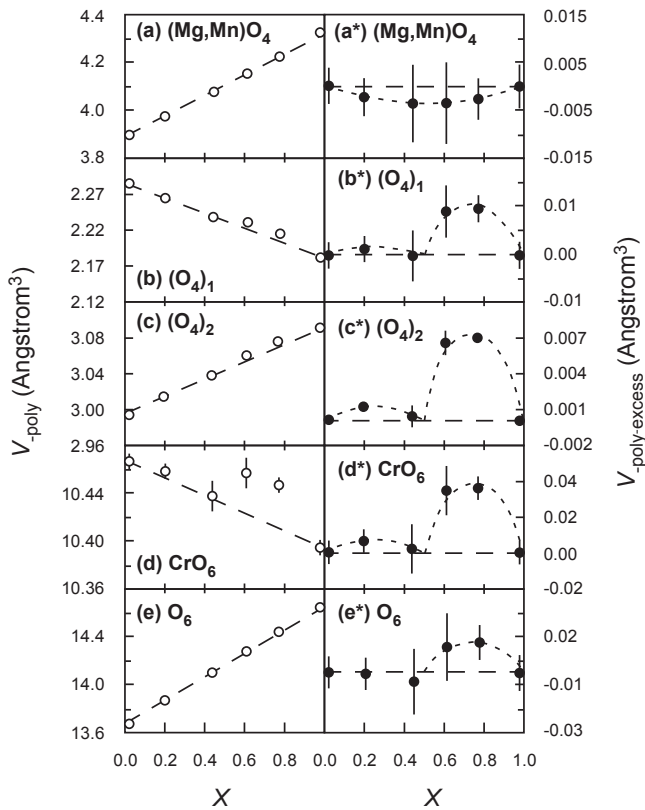
Fig. 8. Correlations between the polyhedral volume (V_{-poly}) and x ((a) (Mg,Mn) O$_4$, (b) (O$_4$)$_1$, (c) (O$_4$)$_2$, (d) CrO$_6$ and (e) O$_6$), and between the $V_{-poly-excess}$ and x ((a*) (Mg,Mn)O$_4$, (b*) (O$_4$)$_1$, (c*) (O$_4$)$_2$, (d*) CrO$_6$ and (e*) O$_6$) of the $(Mg_{1-x}Mn_x)Cr_2O_4-Sp_{ss}$ (ambient P and T). Data at $x = 0$ and 1 are slightly shifted horizontally to display them more clearly. The broken lines represent ideal mixing whereas the dash lines were eye-fitted according to our calculated results.

As x increases from 0 to 1, the volumes of the unit cell, the tetrahedra (the MgO_4, $(O_4)_1$ and $(O_4)_2$) and the octahedra (the CrO_6 and O_6) increase by similar amounts (i.e., 3.75%). The volume of the individual $(O_4)_1$ tetrahedron or CrO_6 octahedron decreases in fact (Fig. 8b and d), but is readily over-compensated by the MgO_4 and $(O_4)_2$ tetrahedra (Fig. 8a and c), or by the O_6 octahedron (Fig. 8e), respectively. The oxygen array continuously deforms further (Fig. 7a). The $(Mg_{1-x}Mn_x)$ Cr_2O_4–Sp_{ss} with $x < 0.5$ have smaller compliance in promoting the Mg–Mn substitution than those with $x > 0.5$, as indicated by the u-excess-x curve (Fig. 7b) and the V-poly-excess-x curves (Fig. 8b*– e*).

4. Implication

In order to accurately constrain the chemical composition and geophysical behavior of the interior of the Earth, precise determinations of the K_T for the constituent minerals with relevant compositions are important. With recent rapid development of some experimental techniques, especially the synchrotron-based high-P techniques, a huge body of data with increasing accuracy has been generated. Due to the large variety of the mineral species and the complex of their compositions, some extrapolation or interpolation with the assumption of a generally linear compositional dependence of the K_T is presently still employed in many cases. For such cases, our study implies that great precaution must be taken since the factors affecting the compressional behavior of mineral solid solutions have not been fully understood.

Many factors, including but not limited to the structure feature of the solid solutions (Hazen and Finger, 1979), the size mismatch of the substituting cations (O'Neill and Navrotsky, 1984), their charge difference (Fe^{3+} versus Ti^{4+} in $Fe_{3-x}Ti_xO_4$–Sp_{ss} for example; Yamanaka et al., 2013), and their electronic and magnetic contrast (Mg^{2+} versus Fe^{2+} in $(Mg_{1-x}Fe_x)_2SiO_4$–Ol_{ss} for example; Dachs et al., 2007), can affect the mixing behavior of a solid solution series, affect the K_T, and affect the correlation pattern of the K_T and composition.

For the crystal structures with extensive edge sharing between the component polyhedra, the size mismatch of the substituting cations is important in determining the relationship between the K_T and composition of a series of solid solutions: if the size difference is small, it has a high tendency to be linear; otherwise, it may be complicated. As demonstrated for the Sp structure, the size difference of the Mg^{2+} and Fe^{2+} in the $(Mg_{1-x}Fe_x)_2SiO_4$–Sp_{ss} is relatively small (~3.5%; O'Neill and Navrotsky, 1983), the K_T has an almost linear dependence to the x (Liu et al., 2016). In comparison, the size difference of the Mg^{2+} and Mn^{2+} in the $(Mg_{1-x}Mn_x)$ Cr_2O_4–Sp_{ss} is somewhat large (~12%; O'Neill and Navrotsky, 1983), the K_T and x have a non-monotonic relationship. Similar phenomenon has also been observed for the Grt structure: for the $(Mg_{1-x}Fe_x)_3Al_2Si_3O_{12}$–$Grt_{ss}$ (~3.4% difference in the sizes of the Mg^{2+} and Fe^{2+}; Shannon, 1976), the correlation between the K_T and x is nearly linear (Huang and Chen, 2014); for the $(Mg_{1-x}Ca_x)_3Al_2Si_3O_{12}$–$Grt_{ss}$

(~25.8% difference in the sizes of the Mg^{2+} and Fe^{2+}; Shannon, 1976), the correlation between the K_T and x is "W"-shaped (Du et al., 2015). This hypothesis seems applicable to the $(Mg_{1-x}Fe_x)O$ periclase-wüstite solid solutions as well, as a generally linear correlation has been observed between the K_T and x (Fei, 1999; an ~3.5% difference in the cation sizes (Shannon, 1976)). For less tightly-bound crystal structures such as the pyroxene and feldspar, on the other hand, the size mismatch of the substituting cations is presumably less important in determining the correlation between the K_T and composition, which is usually monotonic with small curvature. This proposal has been supported by the experimental observations along the $NaAlSi_2O_6$–$CaFeSi_2O_6$ join and $NaAlSi_3O_8$–$CaAl_2Si_2O_8$ join which involve substituting cations with a large range of cation size differences (Angel, 2004; Nestola et al., 2008). For the least tightly-bound or open crystal structures like the olivine and apatite, further, the size mismatch of the substituting cations is usually unimportant in determining the correlation between the K_T and composition, which is commonly linear. For example, the size difference of P^{5+} and V^{5+} in the Pb_{10} $[(PO_4)_{1-x}$ $(VO_4)_x]_6$-F_2–Ap_{ss} is as large as ~108.9% (Shannon, 1976), and the K_T and x relationship has been established as generally linear (He et al., 2012). For the $(Mg_{1-x}Fe_x)_2SiO_4$–Ol_{ss}, the cation size difference is small and the K_T and x relationship is linear (Poe et al., 2010; Nestola et al., 2011a, 2011b), matching the expectation.

Other factors like the charge difference, electronic distinction and magnetic contrast are usually associated with the substitution of different cations with different sizes, so that their effects on the correlation pattern between the K_T and composition are hard to separate and much less well constrained experimentally. O'Neill and Navrotsky (1983) had some discussions on the electronic entropy in the transition-metal Sp, and pointed out that the electronic entropy might affect the cation distribution between the tetrahedra and octahedra in a complicated way. Dachs et al. (2007) delicately constrained the electronic and magnetic contributions to the molar entropy of mixing for the $(Mg_{1-x}Fe_x)_2SiO_4$–Ol_{ss}, demonstrated their importance, and claimed that they might make the thermodynamic behavior of the Ol_{ss} very complicated. Apparently much more work is required before the effects of these factors on the relationship between the K_T and composition can be adequately understood.

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