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Gamma resonance of ^{57}Fe in grunerite at high pressures

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ABSTRACT

Gamma resonance of ^{57}Fe (Mössbauer effect) in natural grunerite was studied at six different pressures up to 8.5 GPa. The isomer shifts δ and quadrupole splittings ΔE_Q of the two resolved paramagnetic Fe^{2+} doublets change significantly: ΔE_Q of the M1, M2, and M3 positions decreases by 2.9%, and ΔE_Q of M4 increases by 21% with increasing pressure; δ of M1, M2, and M3 decreases and δ at M4 increases with increasing pressure, indicating a crossover at about 10 GPa. Linear relationships between δ, ΔE_Q, and pressure and between δ and ΔE_Q were found at 293 K. At pressures smaller than about 1 GPa, the electronic structure of Fe^{2+} in M positions is practically independent of the compression of the unit cell.

Fe^{2+} remains in high-spin configuration up to at least 8.5 GPa. The nuclear electron density of Fe^{2+} in M1, M2, and M3 increases, whereas that in M4 decreases. The changes of δ(M1,M2,M3) and ΔE_Q(M1,M2,M3) are mainly attributed to electronic changes in the Fe^{2+} valence shell and overlap with the ligands. The increase of δ(M4) is ascribed to 4s, 3d electron transfer. For the change of ΔE_Q(M4) the lattice contribution is predominant. The electronic states of Fe^{2+} in the M octahedra become more similar and the M4 octahedra less distorted at high pressures.

INTRODUCTION

Amphiboles are widely occurring minerals in igneous and metamorphic rocks; grunerite $(Fe,Mg)_7Si_8O_{22}(OH)_2$ belongs to the simplest group from a structural and chemical point of view. The crystal structure of grunerite (Finger, 1969) consists of corner-linked tetrahedral double chains connected by ribbons of edge-sharing octahedra. There are four crystallographically nonequivalent octahedral positions, which are designated as M1, M2, M3, and M4. In the end-member Fe/(Fe + Mg) = 1, Fe^{2+} is the only cation at octahedral positions. In Mg-bearing grunerite Fe^{2+} exhibits preference for M4 (Hafner and Ghose, 1971). The M octahedra can be divided into two groups according to their polyhedral geometries: M1, M2, M3 are more or less close to a regular octahedron, whereas M4 is strongly distorted.

Experimental studies on grunerite concerned mostly phase relations (e.g., Gilbert et al., 1982; Lattard and Evans, 1990). Magnetic properties were reported by Linares et al. (1983) and Ghose et al. (1987). The present work was carried out using the same sample as for determination of the compressibility of grunerite (Zhang et al., 1992).

The purpose of this study was to investigate the ^{57}Fe hyperfine parameters, in particular isomer shift δ and nuclear quadrupole splitting ΔE_Q at the structurally distinct positions of Fe^{2+} under high pressures by use of ^{57}Fe Mössbauer effect. This allows study of the effects of pressure on the electronic structure of Fe^{2+}, bonding state, and polyhedral distortion. The results may be compared with those obtained from Ca-rich clinopyroxenes (Zhang and Hafner, 1992) and correlated with the bulk compression of the unit cell. They should also provide data for possible theoretical ab initio calculations from crystal structure.

EXPERIMENTAL DETAILS

Sample

The grunerite sample used in this study was collected in metamorphic rocks of greenschist to low amphibolite facies in the Gongchangling iron mine, China (Chen et al., 1984). The chemical composition is $(Na_{0.05}K_{0.01}Fe^{2+}_{5.33}Mg_{1.46}Fe^{3+}_{0.14}Al_{0.01})$ for the seven M positions, $(Si_{7.92}Al_{0.08})$ for the eight tetrahedral positions, and $(O_{22},OH_{1.92},F_{0.05},Cl_{0.01})$ for the anions (Chen et al., 1984). A detailed description of the paragenesis as well as physical properties are given in Zhang et al. (1992). For the ^{57}Fe gamma resonance experiments, a hand-picked sample was finely ground in acetone and then studied by X-ray diffraction. No impurity was detected.

Gamma resonance of ^{57}Fe at high pressures

A high-pressure cell using the clamp technique was employed as described in detail by Zhang and Hafner (1992). The pressure gradient in the sample area (0.07 cm^2) was approximately 0.07 GPa at 3 GPa and 0.4–0.5 GPa at 7.3 GPa. The error in the pressure determination was estimated to be 0.1–0.5 GPa.

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The transmission spectra at high pressures were recorded with a ^{57}Co/Rh point source of approximately 10-mCi activity. Source and absorber were maintained at 293 K. A sample weighing about 8 mg was used for a high-pressure experiment. A total count rate of approximately 10^6 per channel was accumulated in each spectrum. Data were registered and processed as described by Zhang and Hafner (1992).

Different fitting procedures were tested for the spectra: (1) fitting of two doublets, (2) fitting of one doublet to the two inner lines and single lines to the two outer lines of the spectrum, and (3) fitting of four single lines. The hyperfine parameters derived by the different fitting procedures were essentially identical within experimental error. For the final results, the two inner lines of the spectrum were fitted by a doublet (intensities and widths constrained to be equal) and the two outer lines individually. Because of the somewhat different line widths of the outer lines, it was not possible to fit the Hamiltonian of the quadrupole interaction as performed for $Ca(Fe,Mg)Si_2O_6$ (Zhang and Hafner, 1992).

RESULTS

The paramagnetic γ resonance spectrum of Fe^{2+} in grunerite at ambient conditions consists of two apparent doublets. The doublet with the larger splitting is ascribed to Fe^{2+} in M1, M2, and M3 and that with the smaller splitting to Fe^{2+} in M4. In the following the doublets are labeled with the subscripts 123 and 4, respectively. The δ and ΔE_Q of the doublets of our grunerite sample under ambient conditions are in agreement with previously published data (Hafner and Ghose, 1971). The spectra do not change significantly with increasing pressure up to 8.5 GPa. An invariable fraction of resonant absorption due to traces of Fe^{3+} could be observed in all the spectra. It was ignored in the fits of the Fe^{2+} doublets. Two typical spectra, one at ambient conditions and one at 8.5 GPa, are shown in Figure 1.

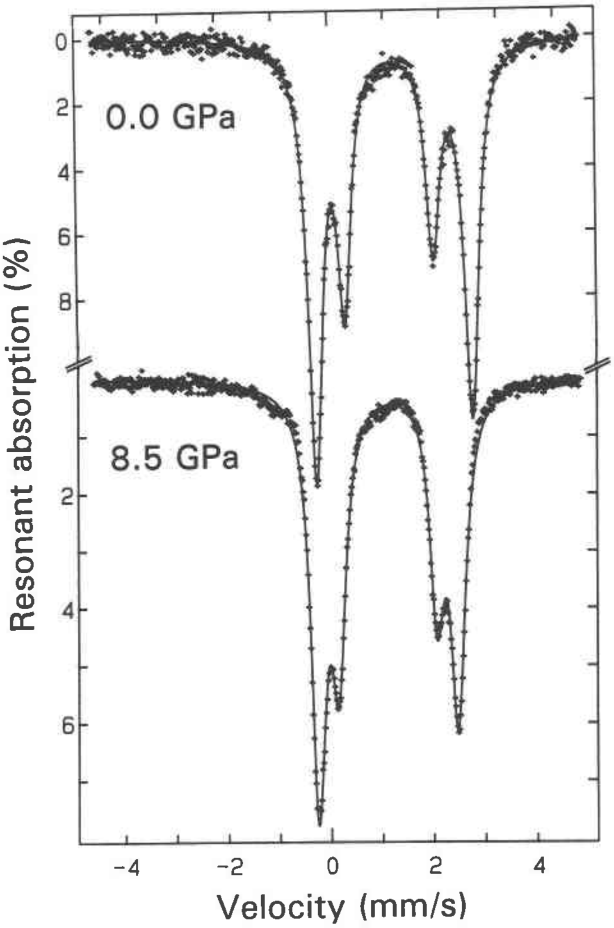

Fig. 1. The ^{57}Fe resonance spectra of grunerite at ambient pressure and 8.5 GPa.

The shift δ of the geometrical center of a Fe^{2+} doublet relative to a fixed Doppler velocity may be written as

$$\delta(T,P) = \delta_0(P) + \delta_{SOD}(T,P) \qquad (1)$$

and its pressure derivative at constant temperature as

$$(\partial\delta/\partial P)_T = d\delta_0/dP + (\partial\delta_{SOD}/\partial P)_T. \qquad (2)$$

In Equations 1 and 2, δ_0 is the chemical or isomer shift at 0 K and δ_{SOD} the second order Doppler shift. Values for δ_{SOD} of Fe^{2+} at M positions in amphiboles at ambient conditions are not well known. Considering the similar geometries of M polyhedra in amphiboles and pyroxenes, δ_{SOD} is expected to be similar in both types of chain silicates. In orthopyroxene, δ_{SOD} at ambient conditions is approximately -0.23 mm/s (cf. Lin et al., in preparation). The $\partial\delta_{SOD}/\partial \ln V$ at constant temperature may be calculated using the Grüneisen parameter γ in the same way as for hedenbergite (Zhang and Hafner, 1992). For grunerite it was obtained by use of the volume compressibility β determined for the same grunerite sample studied in this work (Zhang et al., 1992). The heat capacity C_V was approximated by calculating C_P for tremolite according to Krupka et al. (1985). The thermal expansivity α of tremolite from Sueno et al. (1973) and the Debye temperature θ_D of tremolite from Kieffer (1985) were used. The value of $\partial\delta_{SOD}/\partial \ln V$ obtained in this way was 0.0904 mm/s, corresponding to a value of $\Delta\delta_{SOD} \approx 0.007$ mm/s between ambient pressure and 8.5 GPa. The value of $\partial\delta_{SOD}/\partial \ln V$ of grunerite may be compared with 0.15–0.57 mm/s for hedenbergite (Zhang and Hafner, 1992). The value is small compared with the total pressure shifts of 0.49(9) mm/s for $\partial\delta_{123}/\partial \ln V$ and 0.37(8) mm/s for $\partial\delta_4/\alpha \ln V$. Therefore, no correction was applied to δ, which is regarded as the isomer shift in this work.

The values of δ and ΔE_Q of the Fe^{2+} doublets determined at various pressures and 293 K are listed in Table 1. The values of δ_{123} and ΔE_{Q123} decrease with increasing pressure by approximately 0.05 mm/s and 0.08 mm/s (3%), respectively, between ambient pressure and 8.5 GPa. However, δ_4 and ΔE_{Q4} behave differently: δ_4 increases slightly by 0.03 mm/s and ΔE_{Q4} pronouncedly by 0.33 mm/s (21%) in the same pressure range. Linear least-

TABLE 1. Hyperfine parameters of ^{57}Fe in grunerite between 0 and 8.5 GPa (293 K)

	M123			M4			Area		
Pressure (GPa)	δ* (mm/s)	ΔE_Q (mm/s)	Γ** (mm/s)	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	M123 (%)	M4 (%)	χ^2 (%)
0.0	1.159	2.794	0.26† 0.26	1.079	1.579	0.28	61.6	38.4	0.49
1.0	1.156	2.799	0.27 0.26	1.070	1.576	0.30	61.7	38.3	0.84
3.4	1.138	2.779	0.27 0.26	1.086	1.699	0.31	61.7	38.3	0.84
4.6	1.139	2.762	0.28 0.25	1.094	1.744	0.28	62.4	37.6	0.82
6.0	1.132	2.743	0.31 0.28	1.098	1.788	0.28	63.6	36.4	0.89
8.5	1.114	2.714	0.35 0.33	1.107	1.912	0.33	60.7	39.3	1.30

Note: The experimental error of the parameters is estimated to be approximately 0.01 mm/s (Zhang and Hafner, 1992).
* Referred to metallic Fe at ambient conditions.
** Full width at half intensity.
† The upper value refers to the low energy peak and the lower value refers to the higher energy peak.

squares fits to the data give rise to the following relations as shown in Figures 2 and 3:

$$\delta_{123} = 1.159(2) - 0.0052(5)P \qquad (3)$$

$$\delta_4 = 1.073(3) + 0.0040(7)P \qquad (4)$$

$$\Delta E_{Q123} = 2.804(5) - 0.010(1)P \qquad (5)$$

$$\Delta E_{Q4} = 1.55(1) + 0.040(2)P. \qquad (6)$$

In Equations 3–6, δ and ΔE_Q are in mm/s and P in GPa. Extrapolation of δ_{123} and δ_4 leads to a crossover at approximately 10 GPa due to opposite signs of the slopes of Equations 3 and 4, as shown in Figure 2.

It is interesting to note that the line widths Γ_{123} and Γ_4 are more or less unchanged up to 6 GPa. Considering the larger error expected for the line width than for δ and ΔE_Q, the somewhat larger widths at 8.5 GPa may be regarded as almost within the error of those at lower pressures. The relatively invariable line widths at high pressures are in contrast with those observed for clinopyroxenes in the system Ca(Fe,Mg)Si_2O_6, where the line width for Fe^{2+} in the M1 position, e.g., for hedenbergite, increases as much as 51% between ambient pressure and 10 GPa, although the experimental conditions for grunerite and clinopyroxene samples were the same.

DISCUSSION

The opposite slopes in Figures 2 and 3 result from apparently different electronic structures of Fe^{2+} in the two groups of M polyhedra. The geometries of the M1, M2, M3, and M4 polyhedra are well documented at ambient conditions. Whereas the M1, M2, and M3 polyhedra are nearly ideal octahedra, the M4 polyhedron is strongly distorted, the M4-O4 bond being shortened and the M4-O6 bond being elongated (nomenclature cf. Hawthorne, 1981a). These structural features seem to be the basis for the distinct hyperfine parameters of Fe^{2+}. The smaller ΔE_{Q4} accounts for the larger polyhedral distortion, and the smaller δ_4 implies a more covalent participation in the bonding compared with ΔE_{Q123} and δ_{123}, a rule generally applicable to chain silicates.

Pressure dependence of the isomer shift δ

The δ (neglecting δ_{SOD}) may be written as (Gütlich et al., 1978; Zhang and Hafner, 1992)

$$\delta = \alpha \Delta \rho(0) \qquad (7)$$

and

$$\rho(0) = \rho_c^{\text{free ion}}(0) + \rho_{ov}(0) + \rho_{val}(0). \qquad (8)$$

In Equations 7 and 8, α is a nuclear constant with negative sign for ^{57}Fe; $\rho(0)$ is the electron density at the nucleus (density of s electrons); $\rho_c^{\text{free ion}}(0)$ is the 1s, 2s, and 3s (core) contribution of the free Fe^{2+} ion; $\rho_{ov}(0)$ is the overlap contribution $\rho_{ov}(0) = \rho_c(0) - \rho_c^{\text{free ion}}(0)$, where $\rho_c(0)$ is the effective 1s, 2s, and 3s (core) contribution of Fe^{2+}; $\rho_{val}(0)$ is the valence contribution from the 3d, 4s, 4p orbitals of Fe^{2+} and 2s, 2p orbitals of O^{2-}. The values of $\rho_{ov}(0)$ and $\rho_{val}(0)$ depend generally on pressure.

The derivatives $\partial\delta/\partial P$ of Fe^{2+} at M1, M2, and M3 in grunerite and M1 in hedenbergite have the same sign. In both cases, δ decreases with increasing pressure. The decrease of δ_{123} for grunerite may be interpreted in similar terms as that in hedenbergite: increase of $\rho_{ov}(0)$ with increasing pressure (Zhang and Hafner, 1992). The increasing nuclear electron density of Fe^{2+} in these cases may be attributed to the generally similar polyhedral geometries. It should be noted, however, that there is a difference in the magnitudes of the $\partial\delta/\partial \ln V$ values that describe the change in electron density referred to the change in unit-cell volume. The value $\partial\delta_{123}/\partial \ln V = 0.49(1)$ mm/s of grunerite is significantly smaller than $\partial\delta/\partial \ln V = 1.03$ mm/s of hedenbergite. The opposite is expected in view of the bond distances since the average M-O distance of 2.117 Å for M1, M2, and M3 of grunerite (Finger, 1969)

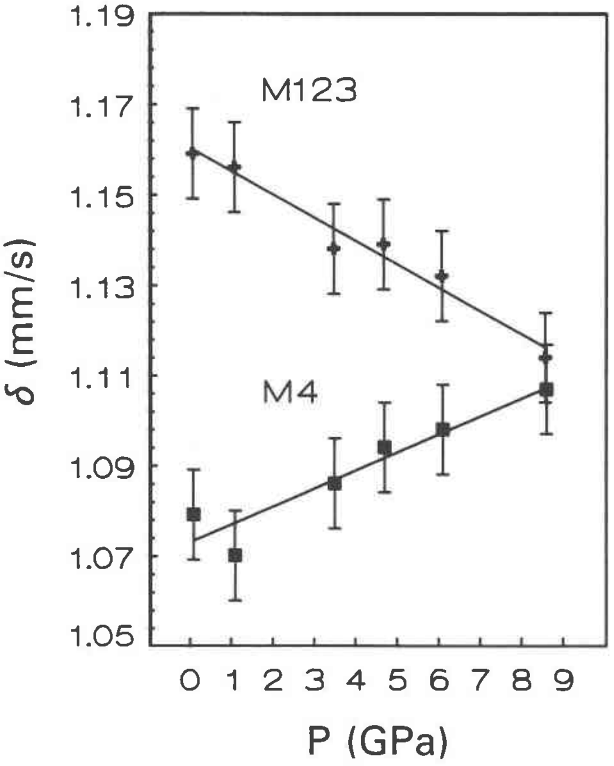

Fig. 2. Pressure dependence of δ.

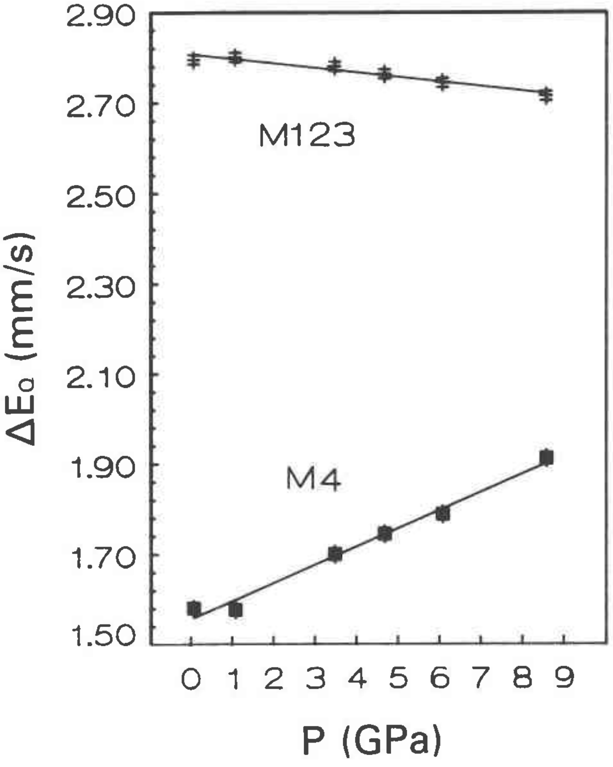

Fig. 3. Pressure dependence of ΔE_Q.

is smaller than that of 2.130 Å for M1 of hedenbergite (Cameron et al., 1973). This behavior may be due to the different compression mechanisms of the two minerals. In hedenbergite, the unit cell and M1 polyhedron exhibit approximately the same compression (Levien and Prewitt, 1981), whereas in grunerite the substantially higher volume compression at pressures lower than about 1 GPa is proposed to be determined primarily by compression of A cavities (Zhang et al., 1992). In that pressure range, the M1, M2, and M3 polyhedra experience little compression.

For the M4 positions, δ_4 increases with increasing pressure as shown in Figure 2. At ambient conditions, δ_4 is smaller than δ_{123} because of the larger term $\rho_{ov}(0)$ due to the increased overlap of 1s, 2s, and 3s orbitals of Fe^{2+} with those of the ligands. The observed positive derivative $\partial\delta_4/\partial P = 3.1 \times 10^{-3}$ mm/s GPa implies that electron transfer from 4s to 3d is the dominant contribution to δ_4 with increasing pressure. On the whole, this results in an increase of shielding of s electrons by d electrons. Assuming that a change in δ_4 is determined primarily by a change in the shortest Fe^{2+}-ligand distance at M4, the slight change in δ_4 with increasing pressure implies a more or less invariable shortest Fe^{2+}-O distance, whereas the average of the Fe^{2+}-O distances at M4 is expected to decrease. At any rate, the net decrease of total nuclear electron density of Fe^{2+} in M4 with increasing pressure is rather small (Fig. 2). This indicates that the bonding character in M4 is changed relatively little at high pressure.

Pressure dependence of the quadrupole splitting ΔE_Q

The ΔE_Q is determined by the maximum eigenvalue V_{ZZ} of the diagonalized second derivative V_{ii} ($i = X, Y, Z$) of the electrostatic potential V at the nuclear position and the asymmetry parameter $\eta = (V_{XX} - V_{YY})/V_{ZZ}$.

V_{ZZ} of high-spin Fe^{2+} is a complex function of the electron density distribution in and around the Fe^{2+} ion. Generally, V_{ZZ} can be separated into three additive terms (Gütlich et al., 1978): (1) the valence contribution V_{ZZ}^{val}, which results from the unbalanced population of 3d orbitals, (2) the lattice contribution V_{ZZ}^{lat}, which originates from the net charges of the ligands and more distant ions in the case of noncubic point symmetry of the crystallographic position, and (3) V_{ZZ}^{ov}, which accounts for the overlap between atomic orbitals of Fe and ligands. It is often difficult to draw conclusions about the relative contributions to the total V_{ZZ} from variations of ΔE_Q alone, although for high-spin Fe^{2+} the dominant contribution of V_{ZZ}^{val} obviously determines the sign of V_{ZZ}. V_{ZZ}^{ov} and V_{ZZ}^{lat} are minor and their signs opposite to the sign of V_{ZZ}^{val}.

One of the surprising results of this study is the fact that the ^{57}Fe doublets of the crystallographically distinct M1, M2, and M3 positions cannot be resolved even at pressures near 10 GPa. The apparent line widths of the doublet due to M1, M2, and M3 remain relatively small over the entire range of pressures (cf. Table 1). The compressibilities of the M1, M2, and M3 polyhedra are, therefore, predicted to be about the same.

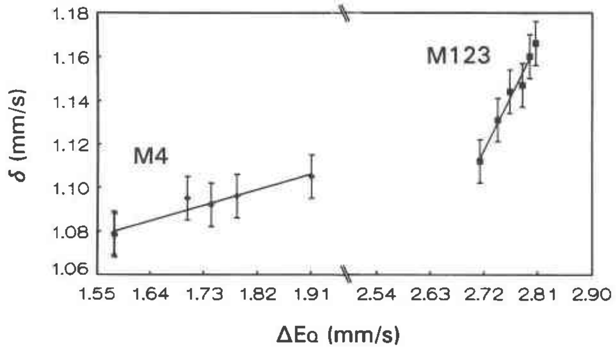

Fig. 4. Linear relationships of δ vs. ΔE_Q for Fe^{2+} at M123 and M4 positions.

Since the M1, M2, and M3 polyhedra are geometrically rather similar, it is reasonable to consider them as a unit for discussing ΔE_{Q123}. Furthermore, taking into account that their polyhedral geometries are comparable to M1 in hedenbergite, the same pseudoaxial symmetries may be used as an approximation for estimating the average energy separation between the $d_{XY,XZ,YZ}$ electronic levels of Fe^{2+} at ambient conditions. This may be done by fitting the ΔE_{Q123} dependence on T between 7 and 293 K using the procedure of Lin et al. (in preparation). A crystal-field splitting Δ was found in this way to be approximately $\Delta \approx 740$ cm^{-1}, which lies on the left side of the maximum of the F function (cf. Fig. 6 in Zhang and Hafner, 1992). From this it follows that the decrease in ΔE_{Q123} with increasing pressure is the consequence of a decrease in V^{val}_{ZZ} related to a decrease of pseudoaxial distortion. A similar behavior was proposed for the M1 position in hedenbergite (Zhang and Hafner, 1992).

The change of 21% in ΔE_{Q4} compared with that of 3% in ΔE_{Q123} between ambient pressure and 8.5 GPa is remarkable. Moreover, it is opposite in sign. It is known that at ambient conditions the M4 polyhedron is considerably distorted from cubic symmetry, resulting in comparatively more covalent bonding. In this case the valence contribution V^{val}_{ZZ} remains effectively invariable (Fig. 6 in Ingalls, 1964). Thus, the change in ΔE_{Q4} may be attributed to a change in V^{ov}_{ZZ} or V^{lat}_{ZZ}. Since the signs of V^{ov}_{ZZ} and V^{lat}_{ZZ} are opposite to that of V^{val}_{ZZ}, the increasing ΔE_{Q4} in our case must result either from the decreasing contribution of V^{ov}_{ZZ} or that of V^{lat}_{ZZ}: either the orbitals of Fe^{2+} overlap less with those of the ligands or the distortion of M4 becomes smaller. It is reasonable to conclude that a predominantly decreasing V^{lat}_{ZZ} must be the reason for increasing ΔE_{Q4} since a decrease of V^{ov}_{ZZ} at high pressures is considered unlikely. In addition, a substantial change in V^{ov}_{ZZ} or in V^{val}_{ZZ} should be coupled with a substantial change in δ_4. This is not the case.

Relationship between δ and ΔE_Q

Figure 4 shows linear relationships between δ and ΔE_Q for the two doublets at pressures up to 8.5 GPa. A similar dependence was observed in Ca(Fe,Mg)Si$_2$O$_6$ clinopyroxenes (Zhang and Hafner, 1992). This is indicative of $\delta - \Delta E_Q$ coupling due to similar changes in electronic structure of high-spin Fe^{2+} in single- and double-chain silicates. It should be noted that the electronic changes in the Fe^{2+} valence shell and the overlap between Fe^{2+} and ligands influence both δ and ΔE_Q, whereas changes in the net charges of the lattice have no direct effect on δ. The changes in δ_{123} and ΔE_{Q123} are mainly governed by related overlap and valence contributions, whereas the relatively drastic change of ΔE_{Q4} hints to a large lattice contribution. This is also reflected in the slopes of the curves in Figure 4. The weak dependence of ΔE_{Q4} on δ_4 clearly suggests that the increase of ΔE_{Q4} is from a dominant decrease of V^{lat}_{ZZ}. The steep slope for M123, however, indicates a large increase of nuclear electron density due to increasing $\rho_{\text{ov}}(0)$.

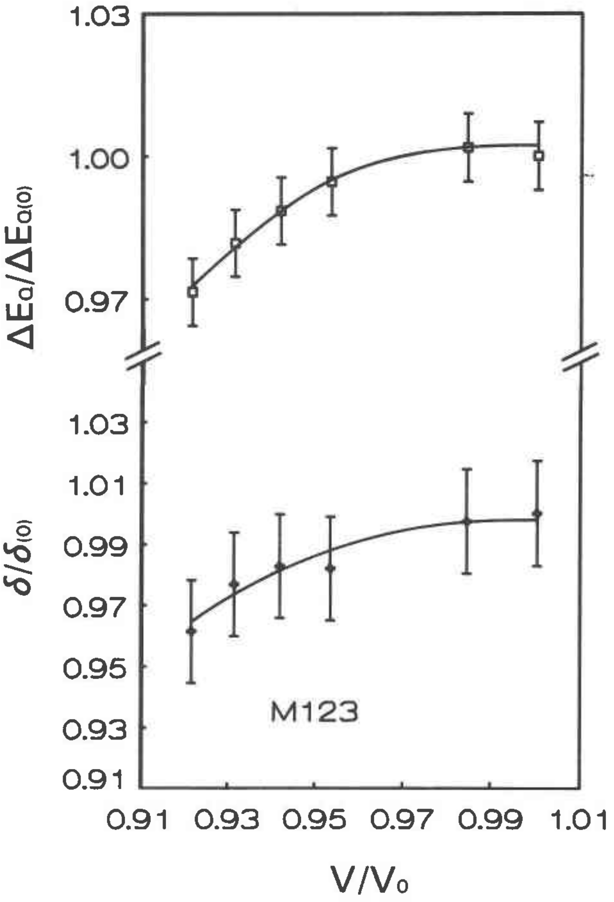

Fig. 5. Normalized δ and ΔE_Q of M123 vs. normalized unit-cell volume.

In iron magnesium manganese amphiboles at ambient conditions, ΔE_{Q4} increases with decreasing Fe/(Mg + Fe) ratio but δ_4 remains nearly unchanged (Hawthorne, 1981b). The same trend was observed in clinopyroxenes of the system Ca(Fe,Mg)Si$_2$O$_6$ (cf. Zhang and Hafner, 1992). It was also observed in anthophyllite for Al^{3+} substitution at M sites (Seifert, 1977). In that system, δE_{Q4} increases and ΔE_{Q123} decreases with increasing Al^{3+} con-

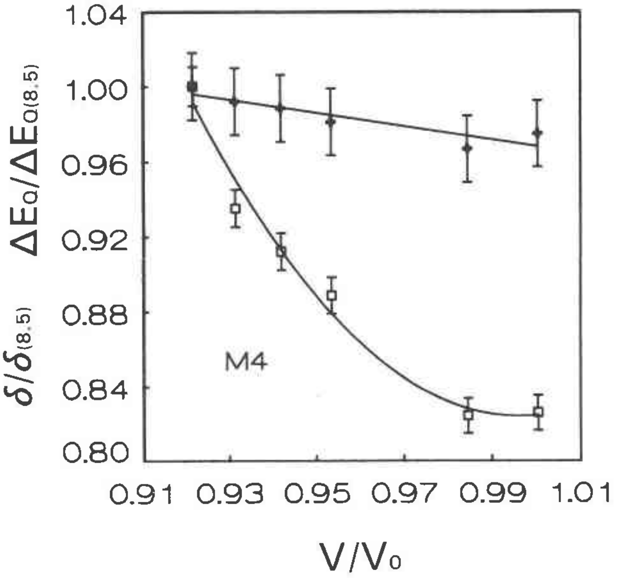

Fig. 6. Normalized δ and ΔE_Q of M4 vs. normalized unit-cell volume.

tent, but δ_4 and δ_{123} remain invariable at ambient conditions. The apparent lack of a δ-ΔE_Q relation implies, however, that V_{ZZ}^{lat} coupled with a change in polyhedral distortion plays the major role in the change of ΔE_Q. Comparison of those data at ambient conditions with the relationships displayed in Figure 4 shows that Al^{3+} substitution is related to the polyhedral geometry determined by the nearest neighbors, whereas pressure has a more complex effect on the ΔE_Q. The same observation has been made for clinopyroxenes of the system $Ca(Fe,Mg)Si_2O_6$ (Zhang and Hafner, 1992).

The simple linear relationships of δ-P and ΔE_Q-P for grunerite (Figs. 2, 3) become nonlinear if the normalized values of δ and ΔE_Q are plotted against the normalized unit-cell volume as illustrated in Figures 5 and 6. An obvious change in slope is observed between 1 and 3.4 GPa. This is especially evident for ΔE_Q. The practically invariable character of δ and ΔE_Q in the lower range of pressures (Figs. 5, 6) means that M1, M2, M3, and M4 polyhedra are not responsible for the reduction of the unit-cell volume at those pressures. From this, it is reasonable to attribute the bulk-volume change primarily to compression of the A cavities, whereas the compression of the M polyhedra at pressures <1 GPa is relatively small.

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