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Comparative crystal-chemistry of mantle silicates and their structural analogs.

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The goal of the study was the detailed investigation of structure and chemical bonding features in Ge-analogs of mantle related silicates. Authors intended to follow the changes in properties of germanates, attended (induced by) the composition or the temperature variation, both at the phase stability fields and at the phase transitions. Three types of structure were distinguished and characterized for the Fe-Mg and Fe-Ca germanates with pyroxene structure using the x-ray and neutron diffraction methods. For the FeGeO_3 , which is the structural analog of the nonretainable high-pressure ferrosilite structure, the neutron diffraction data analysis was completed in the temperature interval 1.7-300K, and two distinct magnetic structures were determined. At 4.2-300K the ^{57}Fe gamma-resonance spectra were investigated for the Fe-Mg and Ca-Fe chain germanates, ferrosilite and hedenbergite, the hyperfine parameters of ^{57}Fe nuclei at M1 and at M2 crystallographic positions were determined.

1. According to results of comparative analysis of topological X-trends "Unit cell parameter – Volume" ($X = \text{Ni, Mg, Co, Fe, Mn, Ca}$) for germanates and relative pyroxenes with orthorhombic (s.g. Pbcn) and with two distinct monoclinic structural modifications (both – with the s.g. C2/c) the structures and the features of their deformation (X-trends) at isomorphous substitution are very close for germanates and corresponding silicates. In particular, as in silicates, two different monoclinic chain structures ("C2/c-I" и "C2/c-II") with the same space group were determined in the Fe-Ca germanates (Fig.1).

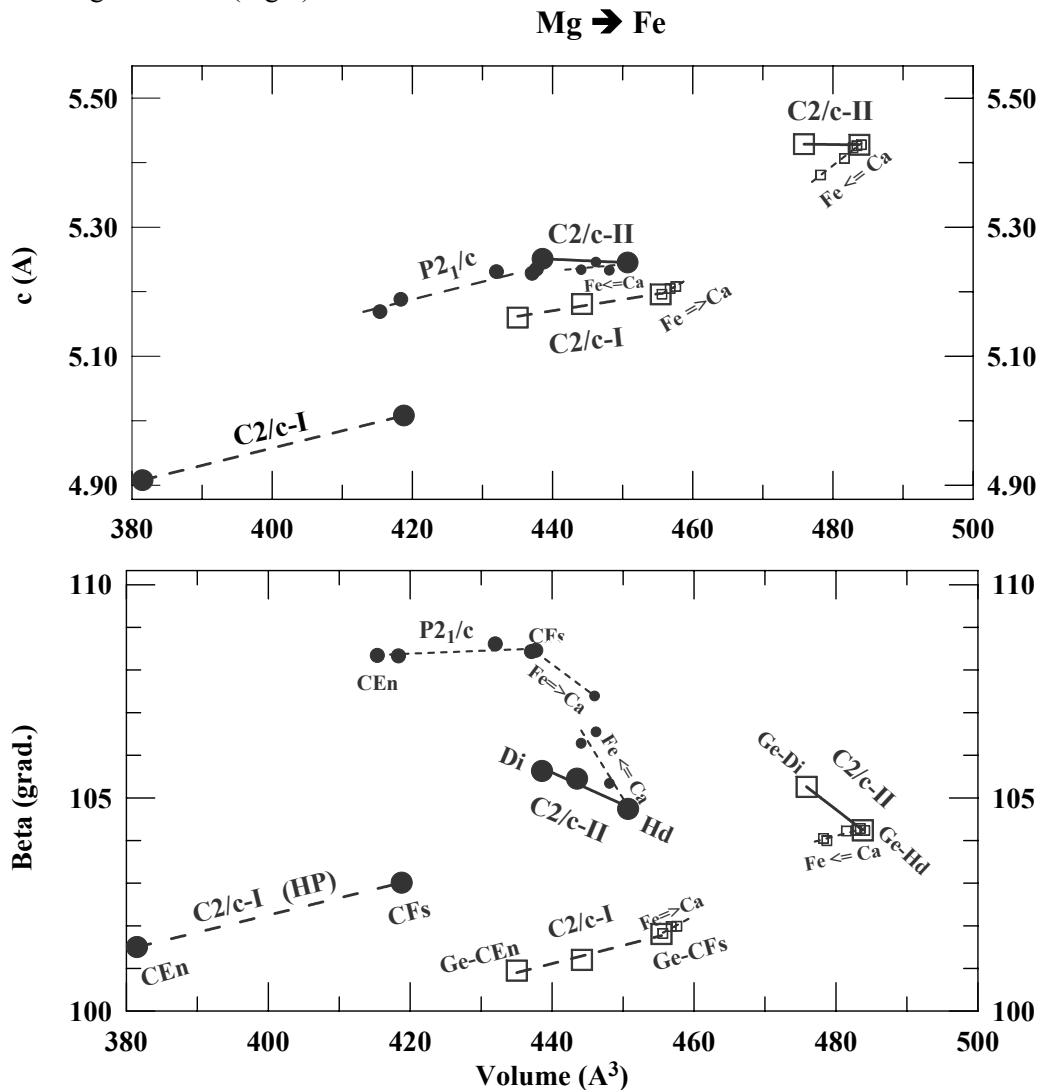


Fig. 1. X-trends “ $c - V$ ” and “ $\beta - V$ ” for the monoclinic (s.g. C2/c) Mg-Fe germanates (squares) and silicates (circles). The modifications “C2/c-I” (dotted line) and “C2/c-II” (line) yield trends with the definitely distinctive character.

The very close features of the X(Mg \Rightarrow Fe) trends for silicates and germanates (along with other data) permit one to propose that as an indirect prove of close physical properties, in particular, to propose close properties of the strain tensors for the germanates and relative silicates. This, in turn, could support the idea to use the structural analogs in tasks of mantle mineralogy.

2. The second goal of the study was to investigate the features of the electron structure of the Fe ions in every of 4 known structural modifications of chain structures, and to determine the possible role of bonds metal – oxygen at phase transitions in pyroxene structures. It was shown, that in all these 4 pyroxene structures, in which Fe ions are “the host – ions” (including nonretainable high-P clinoferrosilite structure) the mean length of the Fe-O bond in the M1 octahedra does not exceed the value of 1.3Å. In any case, the phase transitions “Pbca \rightarrow C2/c-II” and “P2₁/c \rightarrow C2/c-I” at high pressure take place at reaching just this value of the bond length in the “mother” phase. That is why the local field parameters at Fe atoms in the M1 positions were studied in more detailed.

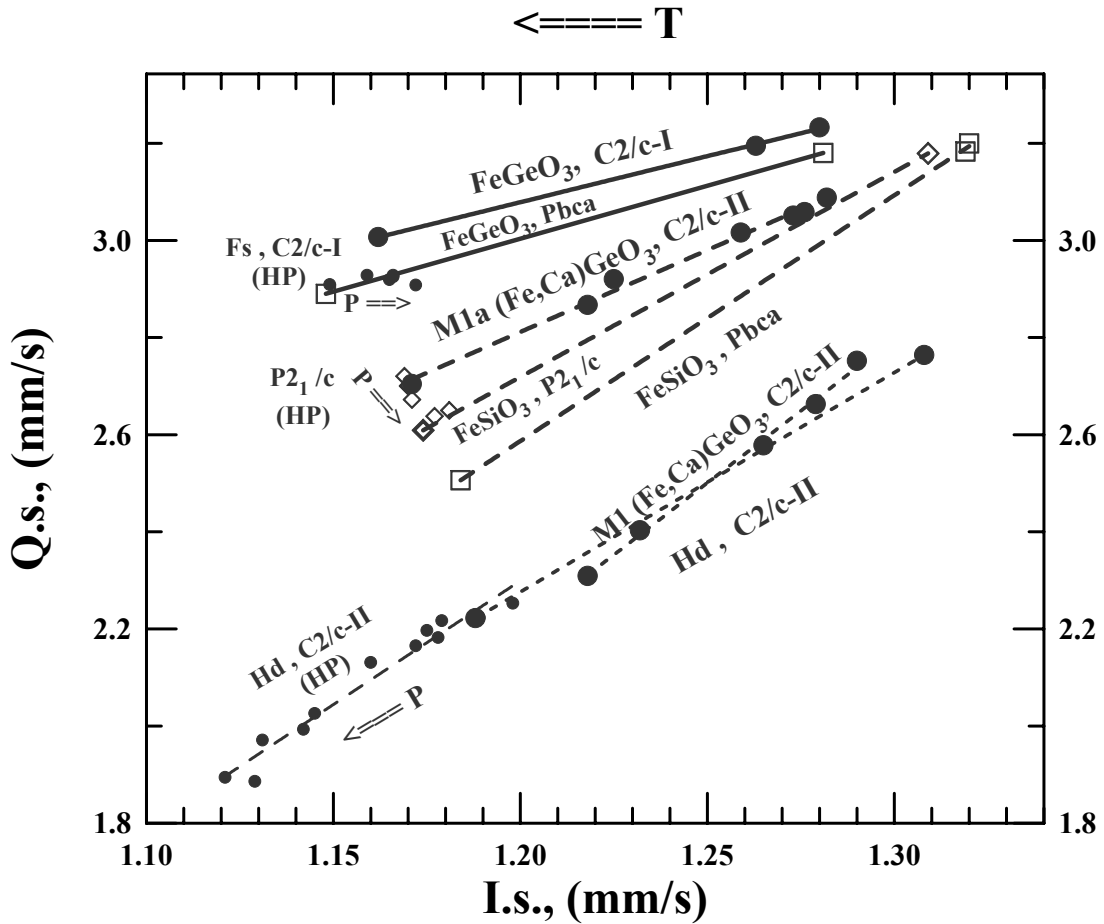


Fig 2. Tree types (“A” – lines; “B” – dotted lines; “C” – short dotted lines) of T – trends “Q.s. – I.s.” for silicates (circles) and germanates (squares) with pyroxene structure. Data at 80K – 300K were used. For the high pressure structures of ferrosilite (“C2/c-I” – small circles, P2₁/c – rhombs) the in situ data (P=1.74 - 3.84 GPa, T=300K, McCammon and C. Tennant, 1996) were used. The in situ data on hedenbergite (Li Zhang and S.S. Hafner, 1992) are presented as well.

For three structural modifications of pyroxenes and their Ge-analogs the comparative analysis of Fe²⁺ electronic structure was performed. It was shown, that the mutual dependence of quadrupole splitting (Q.s.) and the valence electron density on ⁵⁷Fe nuclei (I.s.) is specific enough

to be used both at comparative analysis of the Fe^{2+} electron shells and at the direct identification of the pyroxene structure modification itself.

Using the features of the “Q.s. – I.s.” trends for silicates and germanates with pyroxene structure *three types of electronic structures* of Fe^{2+} ions were distinguished: “C” type – in the structure C2/c-II (hedenbergite and their Ge-analog, short dotted lines); “B” type – in the orthoferrosilite structure and in the high-pressure low-clinopyroxene $\text{P2}_1/\text{c}$ structure, which can be saved by quenching (dotted line); “C” type – in the high pressure monoclinic structure of ferrosilite (C2/c-I), which can not be saved by quenching, and in stable at normal conditions ferrogermanate with the same structure as well in the orthogermanate (line). Three specific types of bonding $\text{Fe}^{2+}-\text{O}$ in M1 positions can be proposed for three types of “Q.s. – I.s.” trends distinguished. Using the “Q.s. – I.s.” trends it was shown, in particular, that in M1 positions of Ca-Fe germanates simultaneously exist two distinct electronic states of Fe^{2+} ions (M1 and M1a, Fig 2.)

In general, the role of chemical bonding just in this positions M1 in pyroxenes is, apparently, very important. According to nuclear gamma-resonance data, at phase transitions $\text{Pbca} \rightarrow \text{“C2/c-II”}$ and $\text{P2}_1/\text{c} \rightarrow \text{“C2/c-I”}$ in pyroxenes and at phase transition $\text{“C2/c-I”} \rightarrow \text{“C2/c-II”}$ in germanates the type of Fe^{2+} electronic structure is changing just in the M1 positions, what is illustrated by T- trends “Q.s. – I.s.” (Fig 2.)

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