

# Pyroxenes: Structural Transformations, Local Fields, and Effects of Short-Range Ordering of Cations

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**Abstract**—To reveal the physical nature of the structural transformations caused by changes in temperature, pressure, or composition, the topological stability of five pyroxene structures of Si–Ge solid solutions was investigated by powder X-ray diffraction. Four structural transformations were provoked by selective substitution of cations, the corresponding changes in local fields in the key structural position *M1* were investigated by Mössbauer spectroscopy.

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Structural transformations in pyroxene Ge–Si solid solutions were provoked by selective substitution of cations in each of three structural cation positions: *M1*, *M2*, and tetrahedra. Si → Ge substitution in tetrahedra radically expands the limits of variation in the unit-cell size, facilitates determination of the limit of geometric stability of pyroxene structures, and clearly reveals different character of their reaction to a change in the average size of cation–oxygen polyhedra in them. The necessity for matching the shared edges and corners of cation–oxygen polyhedra in pyroxenes leads to systematic consequences specific for these chain structures with different elastic properties. This circumstance makes it possible not only to determine the niches of their topological stability, but also gives important information about the nature of structural transformations. In comparative analysis of the structural modifications of monoclinic pyroxenes, we used the method of topological niches: for each structure, the ranges of spread of the unit-cell parameters were determined in the parameter–volume planes ( $a-V$ ,  $b-V$ ,  $c-V$ ,  $\beta-V$ ) [1]. To reveal the physical nature of stimuli of transformations in pyroxene systems, we investigated the distribution of local fields in them.

## NICHES OF TOPOLOGICAL STABILITY OF PYROXENE SYSTEMS

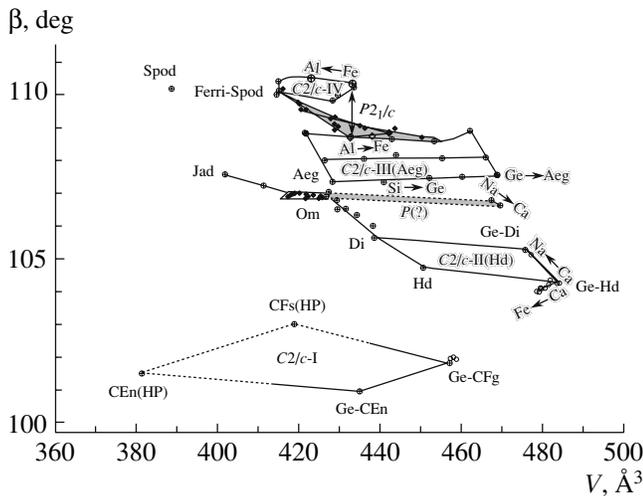
### 1. Alkaline Systems

Two distinguishable monoclinic structures were selected in the  $(\text{Li}_{1-x}, \text{Na}_x)\text{Fe}(\text{Si}, \text{Ge})_2\text{O}_6$  solid solution: five trends of the Si → Ge substitution form pronounced  $\beta$  niches of two different modifications [2]. Figure 1 shows five equidistant  $\beta-V$  trends for five Li/Na ratios. At a large average size of cations in the *M2* position, it is the *C2/c* aegirine structure *C2/c*-III (Aeg) that is stable; its  $\beta$  niche has a shape of a slightly

deformed “half-parallelogram of compositions” of the entire system. The second structure, which is stable at a smaller size of polyhedra *M2*, has a  $\beta$  niche in the form of a cord and is characterized by the space group *P2<sub>1</sub>/c*. The *C2/c*-III → *P2<sub>1</sub>/c* transition is obviously due to the decrease in the size of *M2* polyhedra below the critical value for the aegirine structure (*C2/c*-III in Fig. 1).

When a  $\text{Fe}^{3+}$  ion in the *M1* position is substituted by a smaller  $\text{Al}^{3+}$  ion, the *P2<sub>1</sub>/c* structure in the  $\text{Li}(\text{Fe}, \text{Al})(\text{Si}_y\text{Ge}_{1-y})_2\text{O}_6$  series is retained [3] only at a low content of silicon ( $y < 0.5$ ). The Fe → Al trends (for  $y = 0$  or 0.25) of this structure confirm the expected constancy of elastic response of the *P2<sub>1</sub>/c* structure in the field of its stability. When the critical (for this structure) size of *M1* octahedra is reached, the *P2<sub>1</sub>/c* structure is replaced by a new *C2/c* structure: *C2/c*-IV, with the angle  $\beta$  much larger than for the *C2/c*-III structure. In addition, this new *C* phase, stable at a small average size of octahedra *M1*, differs from *C2/c*-III by elastic response [3] to the substitution of iron ions in *M1* with Al ions; this behavior is confirmed by other trends ( $a-V$ ,  $b-V$ , and  $c-V$ ) [1]. The *C2/c*-IV and *P2<sub>1</sub>/c* structures can coexist (the arrow in Fig. 1) in a narrow composition range [3] (possibly, due to the chemical heterogeneity of the sample).

At simultaneous substitution of ions in all three polyhedra of the  $(\text{Li}, \text{Na})(\text{Fe}, \text{Al})(\text{Si}, \text{Ge})_2\text{O}_6$  solid solution, the field of the  $\beta-V$  plane, covered by the *P2<sub>1</sub>/c* structure, forms a wedge, which separates the niches of the *C2/c*-III and *C2/c*-IV structures. All three structures lose stability with a decrease in the average size of ions in tetrahedra below the critical value (it is likely that each modification is characterized by its own critical value): they are replaced by a tetragonal structure (space group *P4<sub>3</sub>2<sub>1</sub>2*). It is stable (synthesis was performed under normal pressure) in a wide range of com-



**Fig. 1.**  $\beta$  Niches of the three Ge–Si monoclinic Li–Na  $P2_1/c$ ,  $C2/c$ -III, and  $C2/c$ -IV structures; the  $C2/c$ -I structure of high-pressure Fe–Mg pyroxenes of the enstatite–ferrosilite (CEn CFs) series and their Ge analog (Ge-CEn–Ge-CFg); the  $C2/c$ -II structure (Ca–Fe–Mg pyroxenes of the diopside–hedenbergite (Di–Hd) series and their Ge analog); and the general trend niche of the diopside–omphacite–jadeite (Di–Om–Jad) solid solution. The Si  $\rightarrow$  Ge trends of the  $P$  (diamonds) and  $C$  (circles) structures, two Fe  $\rightarrow$  Al trends of the Li–Na–Fe–Al–Si–Ge solid solution with the  $P2_1/c$  structure (enlarged diamonds and circles), and the Ca  $\rightarrow$  Na and Ca  $\rightarrow$  Fe trends of the (Ca, Fe, Na) $FeGe_2O_6$  solid solution with the  $C2/c$ -II structure (diminished circles) are shown.

positions and is changed by narrow extended  $a$ - $V$  and  $c$ - $V$  niches.

## 2. Pyroxene Systems with Divalent Cations

Publication of the data on Ge analogs of Fe–Mg–Ca pyroxenes [1, 4] makes it possible to perform comparative analysis of their structures with a more complete consideration of their specificity and variety. The first group includes monoclinic  $C2/c$  pyroxenes of the Hd–Di series, Ge analogs are known for the end members of this series. The field of stability of this hedenbergite structure in the Ge–Si system is determined by the end members of the  $Ca(Mg,Fe)(Si, Ge)_2O_6$  solid solution. The ( $a$ - $V$ ,  $b$ - $V$ ,  $c$ - $V$ , and  $\beta$ - $V$ ) topological niches have a form of a parallelogram [1], a fact that confirms conservation of the solid solution structure. Figure 1 shows the  $\beta$  niche of this structure:  $C2/c$ -II. The results of the investigation of the  $(Na,Ca)FeGe_2O_6$  and  $(Fe,Ca)FeGe_2O_6$  solid solutions are of particular interest. It was shown in [4] that, in the hedenbergite structure, the substitution of a Ca cation in the  $M2$  position with a foreign one is limited: the Ca  $\rightarrow$  Na and Ca  $\rightarrow$  Fe trends of these germanates exhibit discontinuities. This fact indicates that the end members of these two series belong to different structural modifications and, in particular, justifies the selection of  $C2/c$  hedenbergite and

aegirine structures ( $C2/c$ -II and  $C2/c$ -III, respectively) as different ones.

The second group includes Fe–Mg pyroxenes. Their high-pressure [5] monoclinic  $C2/c$  structure, which is stable only at large values of parameters, was determined a relatively short time ago. Monoclinic Fe–Mg germanates were synthesized and investigated [6]; they turned out to be stable under normal conditions as well. The complete similarity of the elastic reaction to the Fe  $\rightarrow$  Mg substitution (Fig. 1) in the high-pressure structure of silicates and these germanates suggests conservation of the elastic characteristics of this Fe–Mg–Si–Ge solid solution, which is also stable under normal conditions, at least, at partial Ge  $\rightarrow$  Si substitution in tetrahedra. With allowance for the fact that the  $a$ - $V$ ,  $b$ - $V$ , and  $c$ - $V$  trends for the Fe  $\rightarrow$  Mg substitution in the silicate and germanate have similar mutual position [1], we can propose a  $\beta$  niche for the germanate–silicate solid solution in the form of a slightly distorted parallelogram ( $C2/c$ -I in Fig. 1). These considerations complete in general the pattern of topological partition of the  $\beta$ - $V$  plane (Fig. 1).

## 3. Structures with Ions of Different-Valence, Omphacite $P2/n$

In the  $\beta$ - $V$  plane, the structural modifications  $C2/c$ -II and  $C2/c$ -III are separated by the trend niche of pyroxenes (Fig. 1), in which metal cations may have different charges. These pyroxenes belong to the complex Jad–Aeg–(En, Fs)–(Di, Hd) solid solution, associating four crystallochemical minerals with different structures. Among such pyroxenes, we should select omphacites, which differ by their specific properties. They have a monoclinic structure (space group  $P2/n$ ), in which the bands of polyhedra  $M1$  and  $M2$ , as well as the chain of tetrahedra, are divided into two [7]. With allowance for the structural data in the literature for pyroxenes with the general composition Jad–Aeg–Di and the data obtained by us for natural omphacites [8], jadeite and diopside, their total  $\beta$ - $V$  trend is shown in Fig. 1. For these pyroxenes with ions of different valence, three intervals with different types of elastic response of the structure can be selected on the unit-cell volume scale. It is noteworthy that at so large variations in composition the general niche is degenerated into a broken line, on which omphacites occupy the narrowest average interval on the unit-cell volume scale.

Concluding the brief analysis of the revealed topological consequences of the general architecture of monoclinic pyroxene structures, with their necessary chain of rigid tetrahedra, we should note an interesting fact. The aegirine structure  $C2/c$ -III in the  $\beta$ - $V$  plane is separated from one side by a gap from the  $C2/c$ -IV structure, in which the chain of tetrahedra divides into two and a denser  $P$  structure arises, and, from the other side, from the hedenbergite structure ( $C2/c$ -II). As was shown in a direct experiment [4], the Ca  $\rightarrow$  Na trend between the Ge analogs of Hd and Aeg ( $C2/c$ -II and

$C2/c$ -III structures) indeed has a discontinuity (Fig. 1), a fact that directly proves the limited miscibility of these two crystallochemical minals. Note for completeness that the  $\text{Ca} \rightarrow \text{Fe}^{2+}$  trend between the Ge analogs of Hd and high-pressure CFs, belonging to the  $C2/c$ -II and  $C2/c$ -I structures, also exhibits a discontinuity. Study of the local fields in  $M1$  octahedra by Mössbauer spectroscopy significantly clarify this situation.

## LOCAL FIELDS AND STRUCTURE OF PYROXENES

### 1. $\text{Fe}^{3+}$ Ions in Alkaline Pyroxenes

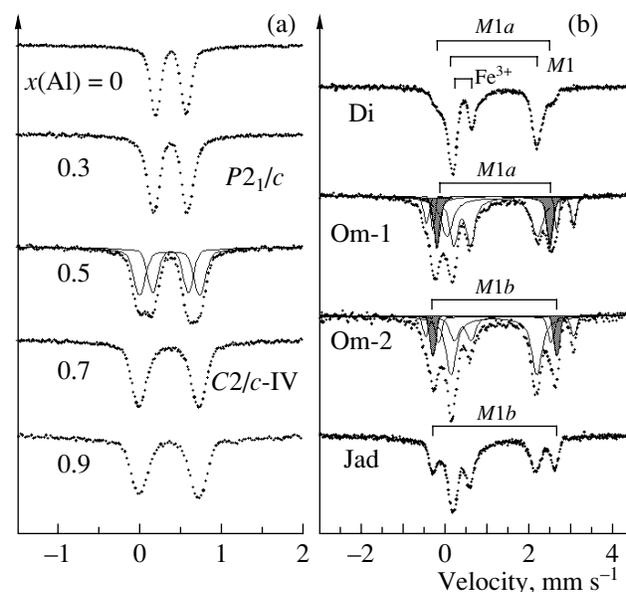
Local Fields and the Shape of  $M1$  Octahedra in the  $C2/c$ -III,  $P2_1/c$ , and  $C2/c$ -IV Structures

Due to the spherical electron shell of the  $\text{Fe}^{3+}$  ions occupying  $M1$  positions in Li–Na pyroxene systems, the  $^{57}\text{Fe}$  nuclei in these ions response specifically to the electric field gradient formed by the nearest oxygen ions. This circumstance gives a convenient tool for detecting changes in the shape of  $M1$  octahedra.

The spectra of the  $\text{Fe}^{3+}$  ions in  $M1$  positions of the  $C2/c$ -III and  $P2_1/c$  structures (Fig. 2a) contain one doublet, and the  $P2_1/c \rightarrow C2/c$ -III structural transition caused by the  $\text{Li} \rightarrow \text{Na}$  substitution in  $M2$  polyhedra does not lead to a significant change in the quadrupole splitting of this doublet. The shape of the  $M1$  polyhedron is retained in this transition. In the fields of stability of each of these two structures, only the dependences of quadrupole splitting on the solid solution composition differ: the dependence for the  $P2_1/c$  structure is much weaker. The isomer shift of the doublet in the spectra of the Li–Na solid solution is independent of the Si/Ge ratio. At the same time, a weak but noticeable systematic decrease in the isomer shift is observed at gradual substitution of Li with Na in  $M2$  positions.

At the same time, the  $P2_1/c \rightarrow C2/c$ -IV structural transition caused by the decrease in the average size of the  $M1$  octahedron at the  $\text{Fe}^{3+} \rightarrow \text{Al}^{3+}$  substitution is pronounced in the Mössbauer spectra (Fig. 2a). Against the background of weak monotonic decrease in the isomer shift in the  $\text{Fe}^{3+}$  ions occupying these positions, which is caused by their substitution with  $\text{Al}^{3+}$  ions, the structural transition is accompanied by a jump in the value of quadrupole splitting. This effect proves that each of these two structural modifications is characterized by its own type of distortion of  $M1$  octahedra. In this case, in the fields of stability of each of the  $P2_1/c$  and  $C2/c$ -IV structures, the hyperfine-structure parameters of  $\text{Fe}^{3+}$  ions change insignificantly. This effect of the average size of ions in the  $M1$  position on the stability of the pyroxene structure and the shape of  $M1$  polyhedra of intrinsic  $\text{Fe}^{3+}$  ions seems to be so distinctly revealed for the first time.

The  $P2_1/c \rightarrow C2/c$ -IV phase transition occurs also at substitution (up to ~30%) of Ge with Si ions in tetrahe-

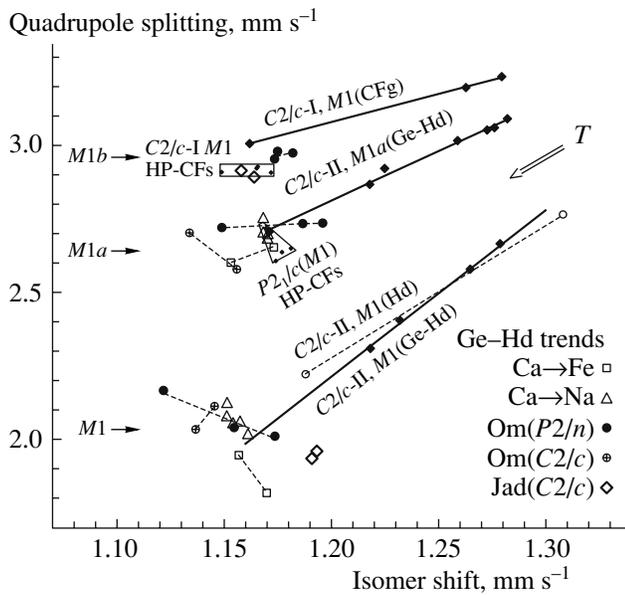


**Fig. 2.** Component-contracted Mössbauer spectra of (a) the  $\text{Li}(\text{Fe}_{1-x}\text{Al}_x)\text{Ge}_2\text{O}_6$  solid solution (and the accepted model of the spectrum of the two-phase sample) and (b) diopside, two omphacites (with the accepted versions of their decomposition), and jadeite.

dra; however, in this case the transition requires a more significant substitution of  $\text{Fe}^{3+}$  ions with  $\text{Al}^{3+}$  ions, which obviously causes further decrease in the average size of  $M1$  polyhedra without changing their shape. The absence of significant broadening of the spectral components indicates the stability and identity of the shape of  $M1$  polyhedra in each of the structures—their distinctive feature in comparison with the Fe–Mg–Ca pyroxenes.

### 2. $\text{Fe}^{2+}$ Ions in Pyroxenes. Effect of the Ions in the $M2$ Position on the Structure of the Polyhedra of the $\text{Fe}^{2+}$ Ions in the $M1$ Position

The  $\text{Fe}^{2+}$  ions in the  $M1$  position in the pyroxenes with dominance of divalent cations are characterized by splitting of the components of their doublet. The nature of the discreteness of local fields and the reasons for this “energy splitting” of the  $M1$  position were investigated in detail in the analysis of the solid solutions of Ca–Fe germanates with hedenbergite structure, in which Ca ions in the  $M2$  position were substituted with  $\text{Fe}^{2+}$  or  $\text{Na}^{1+}$  ions [4]. It turned out that almost a half of Ca ions in  $M2$  positions can be replaced with  $\text{Fe}^{2+}$  or  $\text{Na}^{1+}$  ions without loss of the hedenbergite structure ( $C2/c$ -II in Fig. 1). An additional doublet  $M1a$ , due to  $\text{Fe}^{2+}$  ions, whose relative intensity increases at gradual substitution of  $\text{Ca}^{2+}$  ions in the  $M2$  position with  $\text{Na}^{1+}$  ions [4], was observed in the Mössbauer spectra of such solid solutions, and the origin of this doublet was established (Fig. 3). At such substitution, iron ions can be



**Fig. 3.** Quadrupole splitting–isomer shift  $T$  trends ( $T = 88$ – $300$  K) for the doublets due to the  $\text{Fe}^{2+}$  ions in the  $M1$  position of germanates with the  $C2/c$ -I structure (Ge analog of clinofersilite, doublet  $M1$ ) and the  $C2/c$ -II structure (trends of the  $M1$  and  $M1a$  doublets ( $T = 100$ – $180$  K) for  $(\text{Ca}_{0.8}\text{Fe}_{0.2})\text{FeGe}_2\text{O}_6$  are shown). The  $\text{Ca} \rightarrow \text{Na}$  and  $\text{Ca} \rightarrow \text{Fe}$  concentration ( $X$ ) trends for the  $(\text{Ca},\text{Fe},\text{Na})\text{FeGe}_2\text{O}_6$  solid solution with the  $C2/c$ -II structure and the  $X$  trend, general for jadeites, omphacites, and diopsides, were obtained at  $T = 300$  K. For comparison,  $P$  trends ( $T = 300$  K) are shown for the  $M1$  doublet in the spectra of high-pressure clinofersilite structures  $C2/c$ -I (HP-CFs) and  $P2_1/c$  (HP-CFs) [10].

only in  $M1$  positions; hence, the  $M1a$  doublet observed was attributed to the  $\text{Fe}^{2+}$  ions in the  $M1$  positions having  $\text{Na}^{1+}$  ions in the neighboring  $M2$  positions ( $\text{Fe}^{3+}$  ions also occupy  $M1$  positions). A similar effect is observed in the case of substitution of  $\text{Ca}$  ions in  $M2$  positions with  $\text{Fe}^{2+}$  ions [4], which is explained by the response of the shape of the  $M1$  octahedron to the occurrence of a foreign (for the hedenbergite structure) ion in the  $M2$  position ( $\text{Fe}^{2+}$  in the case under consideration); this response is similar to that noted for another foreign ion:  $\text{Na}^{1+}$ .

### 3. Local Fields in the Pyroxene Structures with Ions of Different Valence, Omphacite $P2/n$

The most interesting example of such pyroxenes is omphacites. Iron ions in omphacites, being guest ones, cannot significantly affect the average size and shape of the  $M1$  and  $M2$  oxygen polyhedra occupied by them and, therefore, the type of the structure and the field of its stability. However, the concept about the role of mutual ordering in the  $M1$  and  $M2$  positions of cations with different charges in the structure of ordered omphacites  $P2/n$ , which is expected to obtain direct

experimental confirmation, makes urgent the question about mutual distribution of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions with respect to the two ions with different charges in the neighboring  $M2$  positions ( $\text{Ca}^{2+}$  and  $\text{Na}^{1+}$ ). The Mössbauer spectrum of omphacites (Fig. 2b) is difficult for analysis: its correct interpretation is hindered by the presence of very closely spaced components. Application of the procedure of component contraction [9] significantly facilitates the problem, and it becomes possible to select in the spectra of omphacites (Fig. 2b) two very close doublets (Fig. 3) with the parameters coinciding with those of the  $M1a$  and  $M1b$  doublets, characteristic of diopside and jadeite, as well as for the  $C2/c$ -II and  $C2/c$ -I structures, respectively [10]. This circumstance allows us to conclude [11] that two different  $M1$ – $M2$ – $T$  cation configurations are present in the omphacite structure  $P2/n$ . One of them is characteristic of the jadeite structure (the  $\text{Al}^{3+}$ – $\text{Na}^{1+}$ – $\text{Si}$  configuration, to which the doublet  $M1b$  of  $\text{Fe}^{2+}$  ions corresponds) and the other is typical of the Di–Hd structure (the  $\text{Mg}$ – $\text{Ca}$ – $\text{Si}$  configuration and the other doublet due to  $\text{Fe}^{2+}$  ions:  $M1a$ ).

The above analysis gives grounds to consider the omphacite structure, which exhibits characteristic signs of three crystallochemical minerals with a limited mutual mixability, as a hybrid structure.

## ACKNOWLEDGMENTS

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