

ADDITIVE MODELS OF OPTICAL PROPERTIES IN MINERALS OF HUMITE POLYSOMATIC SERIES

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Additive models of optic properties of the Mg-F-humite minerals are proposed based on two schemes of structural partition. The recent scheme of structure partition with both forsterite and sellaite layers stacking is discussed and a new one with both norbergite and forsterite layers stacking is suggested. The essence of models is that weighted components of partial dielectric permeability tensors, belonging to different kinds of structural blocks, give an individual pays to average tensor and so they determine refractive indices of mineral. The partial tensor component values were estimated by least squares procedure and the calculated refractive are very close to those. Since both structure partition schemes provide a good agreement with real optical properties for models constructed by them, they seem to be correct and, therefore, the humite group minerals are members of a polysomatic series.

6 tables, 5 figures, 15 references.

Refraction parameters of humite group minerals are subject to appreciable joint influence of isomorph substitutions, both in cationic and anionic matrices of structure. This causes essential overlaps of refraction parameters values of different humite group mineral species.

The attempts to evaluate quantitative influence of chemical composition variations on optical characteristics by experimental data are considered as more or less unsuccessful (Deer *et al.*, 1965, Minerals, 1972).

Theoretical calculations of the average refraction index for magnesium minerals of the group were made by V. Sahama (1953; see in Deer *et al.*, 1965) taking into account the isomorphism $F \leftrightarrow (OH)$ and using polarizability values. These calculations gave the results satisfactorily conformed to experimental data. However, there are deviations successively increasing in the row chondrodite – humite – clinohumite. Refraction index is increased at the same row. In author's opinion, one of the possible steps to solve the above problem is the attempt to construct the additive model of indicatrix parameters variability for this mineral group according to principles discussed in the work by Yu. Punin (1989), that is devoted to optics of heterogeneous layered crystals. The condition of model applicability to humite group minerals is the presence in their crystal structures crystallochemically different layers or blocks, whose quantities changes from one mineral of another. Even now there is no common opinion among mineralogists regarding the existence of such layers or blocks in the crystal structures of humite group minerals (Bragg and Claringbull, 1967, Ribbe and Gibbs, 1969).

The purpose of this work is to construct additive models of optical properties for pure

magnesium-fluorine minerals of the humite group. The results may affect the evaluation of traditional description principles applicability to the crystal structure of humite group minerals as the degree of efficiency of additive model of indicatrix in humite group minerals essentially depends on correct selection of structural fragments.

Optical indicatrix of Heterogeneous crystals

Heterogeneous crystals with irregularities much smaller than the wavelength are optically homogeneous (Punin, 1989). Optical properties of layered heterogeneous crystals are subject to the additivity rule: indicatrices of such crystals depend on volume ratios V_j of structural components characterized by an individual indicatrix and $\sum V_j = 1$. At the first stage, this work has to establish parameters of individual indicatrices for structural components, which contents in various humite group minerals are assumed known.

To solve the problem, we consider Fedorov-Pokkels and Hoiser-Wenk methods the most suitable out of three techniques of resulting indicatrix construction (Punin, 1989). The Mullar method, being convenient for establishment of component volume ratios by optical characteristics of a crystal, in our case should result in appreciable deviations of the form of resulting indicatrix from an ellipsoid. There are no reasons to doubt the ellipsoid form of indicatrices of humite group minerals as anomalies which might evidence the opposite are absent in the accessible publications.

In the Fedorov and Pokkels method (Punin, 1989), tensors of dielectric permittivity of

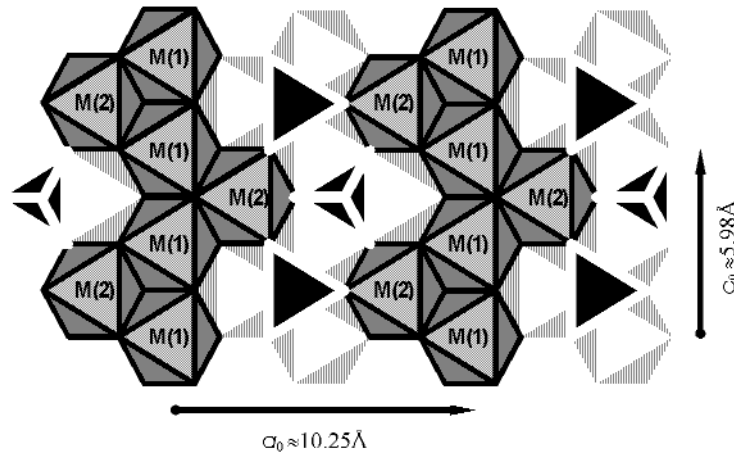


Fig. 1. The idealized structure of forsterite in the Pnam installation, the projection to (010)

components ε_j^{-1} are averaged with the weights equal to volume parts V_j . Main values of resulting tensor $\varepsilon^{-1} = \sum V_j \varepsilon_j^{-1}$ are equal to inverse square values of main refraction parameters – indicatrix semi-axes.

In the Hoiser and Wenk method, tensors of dielectric permittivity of components are exposed to weighted averaging. Squares of main refraction parameters – resulting indicatrix semi-axis – are equal to principal values of the resulting tensor $\varepsilon = \sum V_j \varepsilon_j$.

Application of the optical properties additivity rule to humite group minerals assumes the availability of at least two types of structural components in their structures – diverse layers, which number in a cell changes regularly from mineral to mineral.

Selection of structural components

The most general formula of humite group minerals can be written down as follows (Jones, Ribbe *et al.*, 1969):



were Me = Mg, Fe, Mn, Ca and X = F, OH, and factors f and s – positive counting numbers. Only minerals with s = 1 are currently known. In this case, the composition of titanium-free magnesium members of the group is described by factor f values:

Table 1. Values of factor f in formulas of humite group minerals

| Mineral | Value f |
|-------------|---------|
| Norbergite | 1 |
| Chondrodite | 2 |
| Humite | 3 |
| Clinohumite | 4 |

At the end of the before last century, Penfield and Howe (1894) revealed relations between three known at that time (out of four) magnesium minerals of the humite group. This has allowed to identify variable ratio $\text{Mg}_2[\text{SiO}_4]:\text{Mg}(\text{OH},\text{F})_2$ as a morphotropy parameter. The roentgenostructural studies of all four minerals (Taylor and West, 1928) have shown that structures of humite group minerals are characterized by closest hexagonal packing (CHP) of anions and have much in common with the structure of olivine. Structures were interpreted as combination of forsterite $\text{Mg}_2[\text{SiO}_4]$, and confined between them brucite-sellaite $\text{Mg}(\text{OH},\text{F})_2$ layers, in certain ratios determined for every mineral.

Let's consider this method to distinguish key details in the idealized structure of humite group minerals basing on the system of designations accepted by Bragg and Claringbull (1967). To make comply the orientation of structure of various humite minerals and forsterite, we shall accept a single installation for cells of all minerals as it is proposed in Minerals (1972). In this case, the space group of rhombic forsterite, norbergite and humite will be expressed by symbol Pnam, and space group of monoclinic chondrodite and clinohumite – P12₁/a1. The structures are represent in a projection to (010) in direction [100].

B the idealized forsterite structure (Fig. 1), the CHP plane, as well as in all humite minerals, coincides for the chosen projection with the drawing plane. The filled octahedric positions containing Mg are subdivided into two types – M(1) and M(2). Shown in Fig. 2 (a) forsterite blocks of A and B types are cut out from the forsterite structure and are layers as high as half forsterite c_0 parameter, parallel to

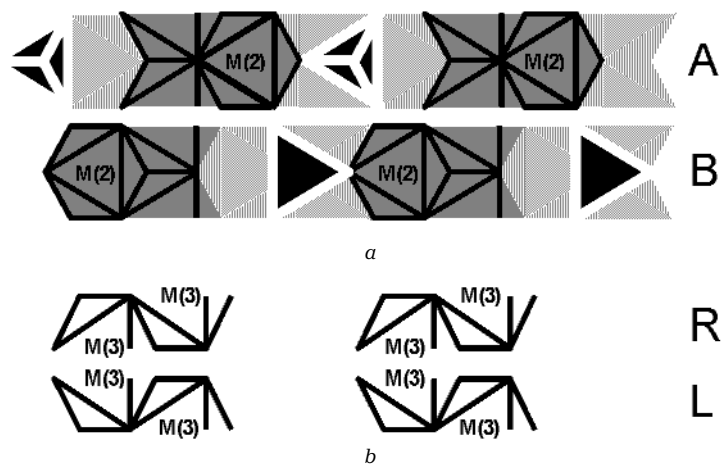


Fig. 2. Separation of structural fragments of the humite group minerals after Bragg (Bragg and Claringbull, 1967), the projection to (010) in the accepted installation: a) forsterite layers A and B, b) sellaite layers R and L

(001) and appear as tapes in the accepted projection.

Brucite-sellaite enantiomorphous blocks R and L (Fig. 2.b) are represented by layers about a quarter of forsterite c_0 thick and contain half-octahedrons of M(3) type. They have a rutile-like structure and can be referred as brucite only because of usual presence of hydroxyl. Blocks are joined in such a manner that R and L never follow in succession whereas blocks A and B may adjoin each other.

If the blocks in the sequence along c^* (hereinafter the vector of inverse lattice) to designate by letters A, B, R and L, than the resulting «words» – cyclic sequences of letters – the following combination rules will be observed: A only follows B or R, B – only A or L, and R and L – only B and A respectively. Each sequence unequivocally defines the mineral, but not on the contrary. Such a system of block designation, as well as blocks itself, N.V. Belov (1976) named Bragg blocks.

The sequence period corresponds to the period along c^* , equal to $c_0 \sin \beta$ of the formed structure. Number of forsterite blocks in the period is always even. Parameters a_0 and b_0 are equal or very close to those of forsterite. In rhombic minerals number of blocks R and L coincides, in monoclinic it is different and the value of difference defines the total shift for the period and affects lattice parameter c_0 and monoclinic angle β . In known monoclinic minerals of the group, the difference is 1. Blocks R should prevail to make the monoclinic angle blunt in the chosen installation and projections for monoclinic minerals. The resulting

ABRL-formulas for magnesium minerals of the group are:

| | |
|-------------|----------|
| Norbergite | ALBR |
| Chondrodite | ABR |
| Humite | ABALBABR |
| Clinohumite | ABABR |

The described scheme to distinguish structural fragments has found wide application and was used by many researchers of humite group, so it could be referred to as traditional. However, having specified the norbergite structure, Ribbe and Gibbs with co-authors (Gibbs and Ribbe, 1969), having confirmed the consistency of results to idealized structures determined by Taylor and West (1928), have made a conclusion that interpretation of structures by the last as an alternation of forsterite and sellaite layers is incorrect and serving a source of mistakes. So, it was found out that traditionally distinguished forsterite and sellaite layers do not correspond to forsterite and sellaite by composition (Jones, Ribbe *et al.*, 1969). Completely denying a possibility and expediency to segregate similar layers, Ribbe, Gibbs *et al.* (1968) consider structures of humite minerals as essentially olivine-like with regular substitution of a part of oxygen atoms in CHP by fluorine and hydroxyl group with formation of vacancies in SiO_4 -tetrahedrons. Zigzag chains of edge-connected octahedrons are accepted as key details of the structure. Are there enough of reasons to completely deny the traditional structure description scheme or its modifications? If there is enough, then the humite group is a morphotropic homological series

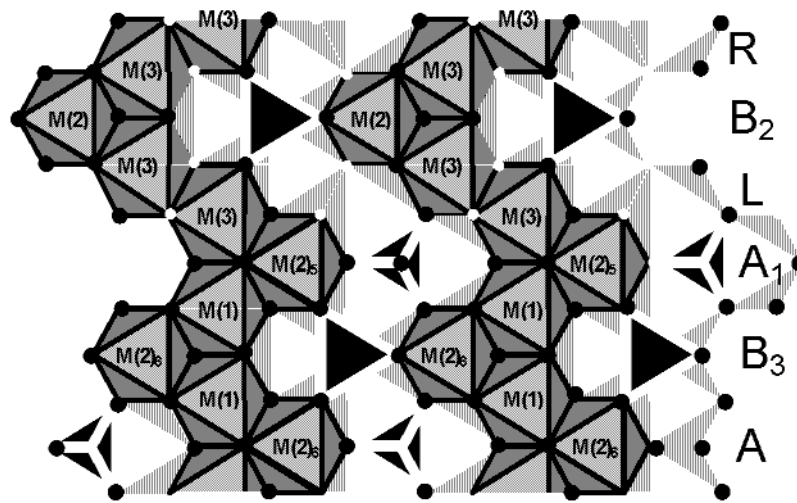


Fig. 3. Differences in the coordination of octahedral positions at various methods of combination ABRL blocks and three kinds of forsterite blocks. ● – Oxygen, ○ – fluorine

complicated by isomorphism, but if it is possible to distinguish blocks, the humite group can yet be considered a *polysomatic series* (Godovikov, 1997).

The analysis of octahedral position coordination features in blocks R(L) and A(B) with consideration of anion differences and options of block combination shows (Fig. 3) that composition of so-called brucite-sellaite blocks R and L is $2\text{Mg}(\text{F},\text{OH})\text{O}$ per cell, as was noted by Jones, Ribbe *et al.* (1969). There is to add that blocks A(B) have diverse composition depending on the surrounding and are subdivided into three kinds (Fig. 3).

In case of a norbergite, forsterite blocks are of kind $A_1(B_1)$, they are surrounded with blocks R and L from both sides. The M(2) octahedron preserves the designation as unique and has two F atoms on the ends of the not divided edge. Semi-octahedrons formed from M(1) octahedrons at cutting blocks A(B) from the forsterite structure are joined with half-octahedrons M(3) of sellaite blocks and resulting octahedrons receive a designation of M(3). Each block of kind $A_1(B_1)$ contributes $2\text{Mg}_2\text{SiO}_3\text{F}^+$ into a cell.

Forsterite blocks contacting with sellaite ones only at one side and adjoining on the other blocks similar to themselves are attributed to kind $A_2(B_2)$. Semi-octahedrons of blocks $A_2(B_2)$ are half-octahedrons M(1) of forsterite, on the contact to block R or L they join half-octahedrons M(3) and this designation is applied to the resulting octahedrons. On the side of forsterite block, half-octahedrons are united with similar ones and are designated

M(1). Octahedrons M(2) of blocks $A_2(B_2)$ on the contact to block R or L have F atom as one of ligands, the position inside such octahedron is designated M(2)₅. The composition of such blocks per cell is $\text{Mg}_4(\text{SiO}_4)\text{SiO}_3\text{F}^+$.

At last, block $A_3(B_3)$ surrounded with blocks $B_2(A_2)$ or $A_3(B_3)$ has a really forsterite composition and does not contain fluorine, its octahedral positions are designated M(1) and M(2)₆. The composition per cell is $2\text{Mg}_2\text{SiO}_4$.

Certainly, it is possible to make twisting boundaries of layers, not dissecting anions half-and-half, but attributing them entirely to one of next blocks and so to avoid formation of charged blocks and to bring compositions of layers to originally declared. But it will not change localization of connections Me-F and Me-O in blocks of different types. However, despite of revealed facts, the ABRL scheme, at due consideration of distinctions between block kinds and elimination of illusions about availability of fragments with sellaite composition and structure, unequivocally sets the composition and structure and correctly transfers topological features of atom coordination. But distinctions in grading blocks A(B) may affect individual contributions of these blocks in optical properties as the connections Me-O and Me-(F,OH) are different, concentrated in different kind blocks in unequal number.

Taking into account the above reserves, let us consider the alternative scheme of block selection (Fig. 4), which results in reduction of kind number to two, if to ignore enantiomorphism as it was made in the traditional scheme. Attaching from both sides to blocks R(L) thin

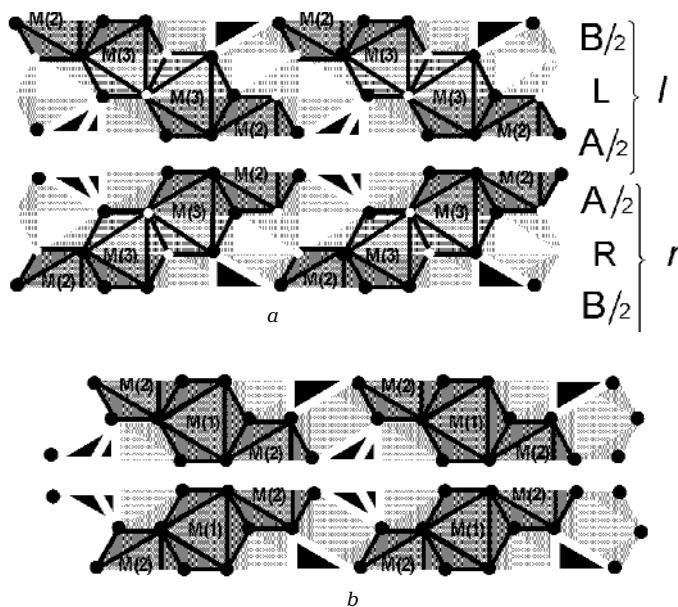


Fig. 4. Structural fragments under the *abrl* scheme: a) norbergite blocks *r* and *l*, b) forsterite blocks *a* and *b*.
● – Oxygen, ○ – fluorine

layers in height of a half-octahedron, separated from buffer blocks A(B), we receive blocks (designated respectively as *r(l)*) having composition of norbergite, in which all F(OH) atoms and connections with their participation are now collected (Fig. 4, a). The payment for this advantage is entry of Si atoms and their connections with oxygen in such blocks.

Two enantiomorphous blocks *a* and *b* of forsterite (Fig. 4, b) could be received by cutting layers from the forsterite structure with a shift by a half-octahedron in comparison with A and B. Such layers contain entirely octahedrons of M(1) and half-octahedrons M(2) positions, which, despite of getting the status of halves of M(2)₅ or M(2)₆ depending on neighbors, do not change the set of atoms and connections within the block. The proposed scheme of block interpretation has no weak points inherent to the traditional scheme and may serve for the description of structure and composition of any humite group mineral as

well as the traditional scheme until minerals with unusual R(L) inserts will be discovered, which is little probable.

Relation of traditional Bragg designations of ABRL sequences of elements to new *abrl* is expressed by the following symbolical formulas: $r = B/2 + R + A/2$, $l = A/2 + L + B/2$, $a = B/2 + A/2$ and $b = A/2 + B/2$, if to keep orientation and sequence of packing along *c*^{*}.

Combination rules change in the appropriate way. It is convenient for both schemes – traditional and proposed – to use the same letter designations to designate the number of different blocks in the period, as for proper blocks; distinctions in the use are easily established from the context. Interesting feature of quantitative ratio in the *abrl* scheme is equality of surpluses (*r-l*) and (*b-a*), whereas $A = B$ in all cases and does not depend on (R-L). Table 2 shows options and quantitative characteristics in traditional and proposed schemes for humite group minerals and fo-

Table 2. Sequence and the maintenance(contents) of structural components in humite group minerals

| Mineral | ABRL-scheme | A + B | R | L | abrl-scheme | a + b | r | l |
|-------------|-------------|-------|---|---|-------------|-------|---|---|
| Norbergite | ALBR | 2 | 1 | 1 | rl | 0 | 1 | 1 |
| Chondrodite | ABR | 2 | 1 | 0 | br | 1 | 1 | 0 |
| Humite | BABRABAL | 6 | 1 | 1 | abrbal | 4 | 1 | 1 |
| Clinohumite | ABABR | 4 | 1 | 0 | babr | 3 | 1 | 0 |
| Forsterite | AB | 2 | 0 | 0 | ab | 0 | 0 | 0 |

rosterite, which is the final member of the polysomatic series forsterite-norbergite. These minerals should be considered as miscible components of the humite polysomatic series because compounds with more than 50 % of Mg(OH,F)₂ are not known and sellaite does not belong to the series.

Volume ratio of structural components, which may be blocks AVR_L or *abrl*, are related to the number of blocks in a cell and thickness of these of blocks. Using data on cell parameters of 10 humite group minerals (Jones, Ribbe *et al.*, 1969) and least-squares method (LSM), we established individual contributions q_j of different blocks in the value of $c_0 \sin \beta$: $q_A = 3.018 \text{ \AA}$, $q_R = 1.354 \text{ \AA}$, $q_a = 3.018 \text{ \AA}$ and $q_r = 4.372 \text{ \AA}$. Root-mean-square deviation (RMSD) of $c_0 \sin \beta$ values calculated with these contributions from experimental values is 0.012 Å. Contributions q_j are evaluations of block thickness and may be considered their relative volumes.

Additive models of the indicatrix

The initial verification of the hypothesis on the additivity of optical indicatrix in minerals of humite polysomatic series was made on synthetic Mg-F representatives of the series, in which isomorph substitutions does not influence optical properties and their relation with the variable contents of structural components is not biased. The properties of synthetic minerals used at calculations were taken from Winchell and Winchell, 1967.

The right crystallophysical system of coordinates XYZ (hereinafter the basic), in which the listed axes coincide with directions of vectors **a**, **b** and **c*** of lattice in the accepted installation, was used for modelling an indicatrix. For rhombic minerals of the group, axis Z is directed by vector **c**, conterminous with direction **c***. In this system of coordinates, the value of main parameters of rhombic minerals will have the

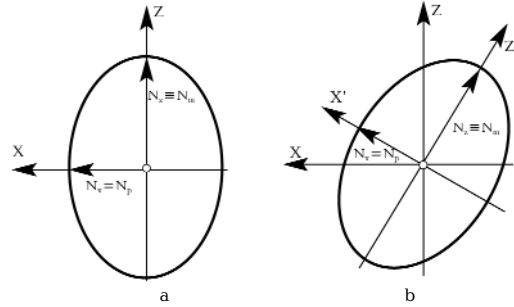


Fig. 5. The indicatrix orientation in relation to the basic axes in the projection to (010): a) rhombic minerals, b) monoclinic minerals

following designations: $N_g = N_y$, $N_m = N_z$ and $N_p = N_x$ (Fig. 5a).

For monoclinic minerals, the same conformities were conventionally accepted, considering that designations are attributed to the transformed system of coordinates X'Y'Z', revolved regarding the basic system around axis X through angle r counted in the positive direction. Taking into account that monoclinic minerals of the group have the N_p axis of indicatrix located in a blunt angle ν , the extinction angle r is negative, that is, the system of coordinates X'Y'Z' for monoclinic minerals is revolved clockwise regarding the basic system (Fig. 5b).

Tensors of impermittivity ϵ^{-1} and permittivity ϵ of orthorhombic minerals in the basic system of coordinates and monoclinic minerals in the X'Y'Z' system have a canonical form, are characterized by three principal values and are noted as

$$\epsilon = \begin{vmatrix} \epsilon_x & 0 & 0 \\ 0 & \epsilon_y & 0 \\ 0 & 0 & \epsilon_z \end{vmatrix}, \quad \epsilon^{-1} = \begin{vmatrix} \epsilon_x^{-1} & 0 & 0 \\ 0 & \epsilon_y^{-1} & 0 \\ 0 & 0 & \epsilon_z^{-1} \end{vmatrix} \quad (1,2)$$

Tensors of monoclinic minerals in the basic system of coordinates get a non-diagonal form related to their principal values

$$\epsilon = \begin{vmatrix} \epsilon_{11} & 0 & \epsilon_{13} \\ 0 & \epsilon_{22} & 0 \\ \epsilon_{31} & 0 & \epsilon_{33} \end{vmatrix} = \begin{vmatrix} \epsilon_x \cos^2 \gamma + \epsilon_z \sin^2 \gamma & 0 & (\epsilon_x - \epsilon_z) \cos \gamma \sin \gamma \\ 0 & \epsilon_y & 0 \\ (\epsilon_x - \epsilon_z) \cos \gamma \sin \gamma & 0 & \epsilon_z \cos^2 \gamma + \epsilon_x \sin^2 \gamma \end{vmatrix}, \quad (3)$$

$$\epsilon^{-1} = \begin{vmatrix} \epsilon_{11}^{-1} & 0 & \epsilon_{13}^{-1} \\ 0 & \epsilon_{22}^{-1} & 0 \\ \epsilon_{31}^{-1} & 0 & \epsilon_{33}^{-1} \end{vmatrix} = \begin{vmatrix} \epsilon_x^{-1} \cos^2 \gamma + \epsilon_z^{-1} \sin^2 \gamma & 0 & (\epsilon_x^{-1} - \epsilon_z^{-1}) \cos \gamma \sin \gamma \\ 0 & \epsilon_y^{-1} & 0 \\ (\epsilon_x^{-1} - \epsilon_z^{-1}) \cos \gamma \sin \gamma & 0 & \epsilon_z^{-1} \cos^2 \gamma + \epsilon_x^{-1} \sin^2 \gamma \end{vmatrix} \quad (4)$$

At absence of absorption, the corresponding main refraction parameters are connected with principal values ε^{-1}_k and ε_k of tensors ε^{-1} and ε at $k = X, Y, Z$, (Modern crystallography, 1981):

$$N_k^{-2} = \varepsilon^{-1}_k \text{ и } N_k^2 = \varepsilon_k. \quad (5,6)$$

Thus, certain values of tensor components correspond to each mineral with measured main refraction parameters. The tensor can be noted in the basic system of coordinates, but this requires knowing the orientation of indicatrix, in particular, the extinction angle r for monoclinic minerals. Using of Fedorov-Pokkels and Hoiser-Wenk methods allows writing down assumed linear dependencies of measured tensor components on evaluated unknown components of individual tensors describing different types of blocks. Definition of components of individual tensors from values of components of the resulting tensors evaluated with the use of measured refraction parameters becomes possible under the condition of availability of preliminary data or assumptions on the form of expression of individual tensors in the basic system of coordinates. Always when connection of components of tensors ε^{-1} and ε with refraction parameters is not directly taken into account, the expressions attributed to tensors of both types — impermittivity and permittivity — are completely similar and to save the room it is enough to result expressions for tensors ε .

Individual optical characteristics of each kind of structural components are described by tensors of the corresponding kind considering the symmetry features of structural

components selected under schemes ABRL and *abrl* and regularities of their quantitative ratios in a cell. As enantiomorphous forsterite blocks A and B always occur in equal number, the same optical characteristic corresponding to a orthorhombic mineral can be formally attributed to any such block. Thus, tensors of blocks A and B in the basic system of coordinates have the canonic form and are characterized by three principal values. Symmetric pairs of individual indicatrices revolved around axis Y of the basic system in opposite directions on equal angles α_R, α_a and α_r regarding axis Z correspond to monoclinic symmetry pairs of enantiomorphous blocks RL, *ab* and *rl*. In the transformed systems of coordinates — revolved regarding the basic system through corresponding angles tensors of monoclinic blocks will have the canonic form and each will be characterized by three principal values. In the basic system of coordinates, tensors of monoclinic blocks get a non-diagonal form and their extra-diagonal components, if not compensated, enter into the resulting tensor of a mineral causing its oblique extinction. We shall only result the corresponding expressions for tensors ε of blocks A(B), R and L as the last two are similar to expressions for others enantiomorphous monoclinic blocks

$$\varepsilon_A = \varepsilon_B = \begin{vmatrix} \varepsilon_{AX} & 0 & 0 \\ 0 & \varepsilon_{AY} & 0 \\ 0 & 0 & \varepsilon_{AZ} \end{vmatrix}, \quad (7)$$

$$\varepsilon_R = \begin{vmatrix} \varepsilon_{R11} & 0 & \varepsilon_{R13} \\ 0 & \varepsilon_{R22} & 0 \\ \varepsilon_{R31} & 0 & \varepsilon_{R33} \end{vmatrix} = \begin{vmatrix} \varepsilon_{RX} \cos^2 \alpha_R + \varepsilon_{RZ} \sin^2 \alpha_R & 0 & (\varepsilon_{RX} - \varepsilon_{RZ}) \cos \alpha_R \sin \alpha_R \\ 0 & \varepsilon_{RY} & 0 \\ (\varepsilon_{RX} - \varepsilon_{RZ}) \cos \alpha_R \sin \alpha_R & 0 & \varepsilon_{RZ} \cos^2 \alpha_R + \varepsilon_{RX} \sin^2 \alpha_R \end{vmatrix}, \quad (8)$$

$$\varepsilon_L = \begin{vmatrix} \varepsilon_{L11} & 0 & \varepsilon_{L13} \\ 0 & \varepsilon_{L22} & 0 \\ \varepsilon_{L31} & 0 & \varepsilon_{L33} \end{vmatrix} = \begin{vmatrix} \varepsilon_{RX} \cos^2 \alpha_R + \varepsilon_{RZ} \sin^2 \alpha_R & 0 & (\varepsilon_{RZ} - \varepsilon_{RX}) \cos \alpha_R \sin \alpha_R \\ 0 & \varepsilon_{RY} & 0 \\ (\varepsilon_{RZ} - \varepsilon_{RX}) \cos \alpha_R \sin \alpha_R & 0 & \varepsilon_{RZ} \cos^2 \alpha_R + \varepsilon_{RX} \sin^2 \alpha_R \end{vmatrix} \quad (9)$$

$$\varepsilon_R + \varepsilon_L = 2 \begin{pmatrix} \varepsilon_{R11} & 0 & 0 \\ 0 & \varepsilon_{R22} & 0 \\ 0 & 0 & \varepsilon_{R33} \end{pmatrix} \quad (10)$$

The diagonal form of the sum of tensors $\varepsilon_R + \varepsilon_L$ corresponds to the rhombic system of minerals of the group with the equal number of blocks R and L, providing compensation of extra-diagonal components of the resulting tensor and, hence, the direct extinction. The equation (10) is also fair for tensors of other pairs of enantiomorphous monoclinic blocks – ab and rl.

The contents of structural components in a cell of i mineral, depending on the used selection scheme of structural components, is characterized by values $(A+B)_i$, R_i and L_i , or a_i , b_i , r_i and l_i (Table 3), which, after multiplication by thickness q_j of corresponding blocks and normalization by the total of all products, represent V_{ji} – volume parts of inputs of j blocks individual tensors into the resulting tensor of i mineral of the group.

At structure interpretations under ABRL and *abrl* schemes, the resulting tensor is represented as follows:

$$\varepsilon_i = V_{(A+B)i} \varepsilon_A + V_{Ri} \varepsilon_R + V_{Li} \varepsilon_L \quad (11.1)$$

$$\varepsilon_i = V_{ai} \varepsilon_a + V_{bi} \varepsilon_b + V_{ri} \varepsilon_r + V_{li} \varepsilon_l \quad (11.2)$$

Equating separate components of the resulting tensor in (11.1) to sums of corresponding components in the right part, with the account of (7), (8), (9) and compensation of extra-diagonal components by equal number of enantiomorphous blocks R and L, we receive for the ABRL scheme

$$\varepsilon_{11i} = V_{(A+B)i} \varepsilon_{AX} + (V_{Ri} + V_{Li}) \varepsilon_{R11}, \quad (12.1)$$

$$\varepsilon_{22i} = V_{(A+B)i} \varepsilon_{AY} + (V_{Ri} + V_{Li}) \varepsilon_{R22}, \quad (12.2)$$

$$\varepsilon_{33i} = V_{(A+B)i} \varepsilon_{AZ} + (V_{Ri} + V_{Li}) \varepsilon_{R33}, \quad (12.3)$$

$$\varepsilon_{13i} = \varepsilon_{31i} = (V_{Ri} - V_{Li}) \varepsilon_{R13}, \quad (12.4)$$

For the *abrl* scheme, in which all separate blocks are monoclinic, equating of separate

components in the left and right parts in (11.2) with the account of (7), (8), and (9) results in more complex dependencies

$$\varepsilon_{11i} = (V_{ai} + V_{bi}) \varepsilon_{a11} + (V_{ri} + V_{li}) \varepsilon_{r11}, \quad (13.1)$$

$$\varepsilon_{22i} = (V_{ai} + V_{bi}) \varepsilon_{ay} + (V_{ri} + V_{li}) \varepsilon_{ry}, \quad (13.2)$$

$$\varepsilon_{33i} = (V_{ai} + V_{bi}) \varepsilon_{a33} + (V_{ri} + V_{li}) \varepsilon_{r33}, \quad (13.3)$$

$$\varepsilon_{13i} = \varepsilon_{31i} = (V_{ri} - V_{li}) (\varepsilon_{a13} + \varepsilon_{r13}). \quad (13.4)$$

Prior to evaluation of individual tensor components, preliminary verification of fulfillment of one elementary consequence of the prospective model was carried out. Fedorov-Pokkels and Hoiser-Wenk methods were simultaneously compared and the second was preferred. Regarding tensors, the rule of trace invariance (Il'in and Pozdnyak, 1984) is observed and values of traces of experimentally established tensors should be rather close to sums of individual tensor traces multiplied by corresponding V_i . For schemes ABRL and *abrl*, conditions of traces equality is received by summarizing (12.1-3) and (13.1-3) respectively:

$$\text{tr}(\varepsilon_i) = V_{(A+B)i} \text{tr}(\varepsilon_A) + (V_{Ri} + V_{Li}) \text{tr}(\varepsilon_R), \quad (14)$$

$$\text{tr}(\varepsilon_i) = V_{(a+b)i} \text{tr}(\varepsilon_a) + (V_{ri} + V_{li}) \text{tr}(\varepsilon_r). \quad (15)$$

Values of traces of tensor ε_i^{-1} of impermittivity $\text{tr}(\varepsilon_i^{-1}) = N_{X_i}^{-2} + N_{Y_i}^{-2} + N_{Z_i}^{-2}$ and traces of tensor ε_i of permittivity $\text{tr}(\varepsilon_i) = N_{X_i}^2 + N_{Y_i}^2 + N_{Z_i}^2$ were substituted in the left parts of equations (14) and (15) according to (5) and (6). Values of individual tensor traces were found by the LSM procedure and resulting tensor traces calculated with these values have shown a good consent with values of ε_i traces, received out of refraction parameters by the Hoiser-Wenk method. The relative RMSD was 0.017 % for both schemes of selecting structural components. For traces of tensors ε_i^{-1} (Fedorov-Pokkels method) relative RMSD is 0.039 %, also for both selection schemes.

Under the ABRL scheme, principal values ε_{AX} , ε_{AY} , ε_{AZ} and ε_{RX} , ε_{RY} , ε_{RZ} of individual tensors ε_A and ε_R were determined by the Hoiser-Wenk method using LSM and equations (12), (8) and (9) with simultaneous formal search of angle

Table 3. Optical characteristics and contents of structural components in Mg-F humite group minerals

| Mineral | $N_x = N_p$ | $N_y = N_g$ | $N_z = N_m$ | $x \angle N_p$ | A+B | R | L | a | b | r | l |
|-------------|-------------|-------------|-------------|----------------|-----|---|---|---|---|---|---|
| Norbergite | 1,548 | 1,570 | 1,552 | 0 | 2 | 1 | 1 | 0 | 0 | 1 | 1 |
| Chondrodite | 1,582 | 1,612 | 1,594 | -22 | 2 | 1 | 0 | 0 | 1 | 1 | 0 |
| Humite | 1,598 | 1,63 | 1,606 | 0 | 6 | 1 | 1 | 2 | 2 | 1 | 1 |
| Clinohumite | 1,608 | 1,636 | 1,618 | -9 | 4 | 1 | 0 | 1 | 2 | 1 | 0 |

Table 4. Refraction parameters of Mg-F minerals of the humite group, designed using individual tensors of blocks under the ABRL scheme

| Mineral | $N_x=Np$ | N_x calc. | $N_y=Ng$ | N_y calc. | $N_z=NM$ | N_z calc.. | $x\angle Np$ | $x\angle Np$ calc. |
|-------------|----------|-------------|----------|-------------|----------|--------------|--------------|--------------------|
| Norbergite | 1.548 | 1.5477 | 1,570 | 1,5704 | 1.552 | 1.5521 | 0 | 0 |
| Chondrodite | 1.582 | 1.5824 | 1,612 | 1,6115 | 1.594 | 1.5931 | -22 | -22.9 |
| Humite | 1.598 | 1.5990 | 1,630 | 1,6284 | 1.606 | 1.6078 | 0 | 0 |
| Clinohumite | 1.608 | 1.6068 | 1,636 | 1,6377 | 1.618 | 1.6171 | -9 | -11.9 |
| RMSD | | 0.0004 | | 0.0006 | | 0.0005 | | 1.52 |

Table 5. Individual refraction parameters of blocks under the ABRL scheme

| Main refraction parameters | | | | | |
|----------------------------|--------|---------------------------|---------------------------|--------|-----------------------------|
| «Sellaite» blocks (calc.) | | Sellaite (Minerals, 1963) | Forsterite blocks (calc.) | | Forsterite (Minerals, 1963) |
| N_x | 1.3519 | 1,381 – 1,390 | N_x | 1.6352 | 1,635 |
| N_y | 1.3338 | 1,370 – 1,378 | N_y | 1.6683 | 1,670 |
| N_z | 1.2991 | 1,370 – 1,378 | N_z | 1.6471 | 1,651 |

α_R , optimal in terms of the minimum sum of square discrepancies of calculated resulting tensors and ϵ_i tensors. The following principal values of tensors ϵ_A and ϵ_R were received: $\epsilon_{AX} = 2.6739$, $\epsilon_{AY} = 2.7863$, $\epsilon_{AZ} = 2.7129$, $\epsilon_{RX} = 1.8276$, $\epsilon_{RY} = 1.7791$, $\epsilon_{RZ} = 1.6877$ and angle $\alpha_R = 72.11^\circ$. The main refraction parameters of four and extinction angles of two minerals calculated using principal values of individual tensors ϵ_A and ϵ_R are well coherent with experimental data (Table 4).

Principal values of individual tensors of blocks A(B) and R(L) allow to estimate their main refraction parameters (Table 5). Difference of these parameters from those of minerals which names are assigned to blocks set under the ABRL scheme was expected because blocks are in interaction and their actual composition does not correspond to their conventional names as shown above.

LSM evaluations of components of tensors ϵ_b and ϵ_r of structural blocks set under the abrl scheme also allow to calculate the main refraction parameters and extinction angles in good accordance with experimental: RMSD of calculated main parameters from N_{x_i} , N_{y_i} , and N_{z_i} are 0.0004, 0.0006 and 0.0006 respectively and 1.33° for the extinction angle. However, the V_{ji} set realized in the used data file, results in unsolvability regarding principal values of tensors, except for $\epsilon_{bY} = \epsilon_{b22}$ and $\epsilon_{rY} = \epsilon_{r22}$. As follows from equation (13.4), inputs of diagonal components ϵ_{b13} and ϵ_{r13} into the resulting tensors ϵ_i are made with identical factors, therefore the data on pure Mg-F minerals of the group only enable evaluation of $(\epsilon_{b13} + \epsilon_{r13})$ which cannot be divided between tensors of blocks b and r. This circumstance does not allow to reduce unequivocally tensors ϵ_b and ϵ_r to the diagonal form and to estimate their principal values ϵ_{bX} , ϵ_{rX} , ϵ_{bZ} and ϵ_{rZ} . Nevertheless, the alone sum $(\epsilon_{b13} + \epsilon_{r13})$ with inherent factors

$(V_{ri} - V_{ji})$ entirely forms extra-diagonal ϵ_{i3} component of the resulting tensor in monoclinic minerals of the group. It allows, using also evaluations ϵ_{b11} , ϵ_{b33} , ϵ_{r11} and ϵ_{r33} , to calculate all parameters of indicatrix, including the extinction angle. Table 6 shows evaluations of component of tensors ϵ_b and ϵ_r .

In case of humite and norbergite – rhombic minerals with direct extinction – contents of blocks and related factors V_{ji} are such that extra-diagonal components ϵ_{b13} and ϵ_{r13} of tensors ϵ_b and ϵ_r have zero value according to (10) or (13.4). Really, at $a = b$ and $r = l$, pair enantiomorphous half-forsterite and half-norbergite monoclinic blocks form quantitative combinations corresponding to rhombic forsterite and norbergite in equal number in humite and, apparently, to rhombic norbergite – in norbergite. Hence, diagonal components ϵ_{b11} , ϵ_{b22} and ϵ_{b33} , ϵ_{r11} , ϵ_{r22} and ϵ_{r33} in themselves set individual main refraction parameters and are principal values of individual tensors ϵ_{fo} and ϵ_n for equivalents of forsterite and norbergite represented in the structure as pair combinations of even spatially separated blocks ab and rl. Table 6 shows individual main refraction parameters for equivalents of forsterite and norbergite corresponding to components ϵ_{fo} and ϵ_n .

Good conformity of these values to actual parameters of forsterite and norbergite is natural as the blocks set under this scheme really have compositions of given minerals and similar structures in the specified pair combinations.

Conclusions

Comparing additive models of indicatrices of Mg-F humite group minerals constructed under two schemes of structural component

Table 6. Components of individual tensors of blocks in the *abrl* model and refraction parameters of forsterite and norbergite equivalents

| Evaluations a component of tensors | Designed refraction parameters of forsterite and norbergite equivalents | Refraction parameters of forsterite and norbergite (Minerals, 1972) | |
|--|---|---|-------|
| $\epsilon_{b11} = \epsilon_{foX}$ | 2.6739 | N_{foX} 1.6352 | 1,635 |
| $\epsilon_{b1Y} = \epsilon_{b22} = \epsilon_{foY}$ | 2.7864 | N_{foY} 1.6692 | 1,670 |
| $\epsilon_{b33} = \epsilon_{foZ}$ | 2.7129 | N_{foZ} 1.6471 | 1,651 |
| $\epsilon_{r11} = \epsilon_{nX}$ | 2.3955 | N_{nX} 1.5477 | 1,548 |
| $\epsilon_{rY} = \epsilon_{r22} = \epsilon_{nY}$ | 2.4663 | N_{nY} 1.5704 | 1,570 |
| $\epsilon_{r33} = \epsilon_{nZ}$ | 2.4089 | N_{nZ} 1.5521 | 1,552 |
| $(\epsilon_{b13} + \epsilon_{r13})$ | 0.02071 | | |

selection, it is possible to state that both models allow to predict optical characteristics of minerals with good precision proceeding from block presentation of their structure. The model under the *abrl* scheme gives a little bit better prediction of the extinction angle for monoclinic minerals. This is well understandable as in the ABRL model extra-diagonal component of the resulting tensor, responsible for oblique extinction, is entirely caused by inputs of blocks R(L), whereas in the *abrl* model the value of extra-diagonal components of the resulting tensor is formed by both norbergite and forsterite blocks. In the latter case, it is impossible to divide this responsibility between them only basing on magnesium-fluorine members of isomorph series. The construction of additive models of optical properties for minerals of the group with isomorphism under schemes $Fe \rightarrow Mg$, $(OH) \rightarrow F$ and $TiO_2 \rightarrow Mg(F, (OH))_2$ is a subject for the further studies and will probably allow to divide influence of various types of blocks on the extinction angle value.

The additive models based on the assumption about cumulative influence of individual properties of structural components set by traditional and proposed in this work techniques on optical properties of a mineral adequately describe variability of indicatrix. This allows to make a conclusion that traditional interpretation of structures of humite group minerals is acceptable. The more correct from the crystallochemical point of view description of the structure gives the *abrl* scheme proposed in this work, which allows to consider humite group minerals as members of a polysomatic series, in which forsterite and norbergite blocks are combined in various proportions.

The constructed models may be used for prediction of optical characteristics of hypothetical minerals of the group, provided that their structure will be presented as a sequence of O or *abrl* blocks.

The author thanks Professor E.I. Semenov, fruitful dialogues with whom initiated this work.

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