ON A SECOND-ORDER PHASE TRANSITION IN THE STRUCTURE OF PHLOGOPITE

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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CRYSTALLOGRAPHY

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ON A SECOND-ORDER PHASE TRANSITION IN THE STRUCTURE OF PHLOGOPITE

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A study of the coefficient of thermal expansion (c.t.e.) of artificial mica $KMg_3[AlSi_3O_{10}]F_2$ (fluorophlogopite) (^{1}) showed that the c.t.e. along the axes a and b has a break at a temperature of $290 \pm 30°$. Above this temperature it decreases. Along the c axis no such changes were observed. The ellipsoid of the mean values of the c.t.e. ($\bar{\alpha}$) is represented in the following form:

Fig. 1. Projection of part of the phlogopite structure onto the plane (001): a —before the phase transition; b—above the temperature of the phase transition

$$\bar{\alpha}_{20-290^\circ} = (9.6C_{13}^2 + 12C_{23}^2 + 17C_{33}^2) \cdot 10^{-6} \text{ deg}^{-1},$$

$$\bar{\alpha}_{290-800^\circ} = (4.0C_{13}^2 + 9.9C_{23}^2 + 17C_{33}^2) \cdot 10^{-6} \text{ deg}^{-1}.$$

The authors of (^{1}) note that the cause of this behavior of the c.t.e. has not at present been explained.

However, this phenomenon can be explained on the basis of the geometry of the mica structure. The break in the temperature dependence of the c.t.e. indicates the presence of a second-order phase transition. Such transitions are often associated with slight changes in the structure. The absence of a break in the c.t.e. along the c axis indicates that such changes exist only in the plane of the a and b axes, (001). The essence of the phase transition in the present case is that the ditrigonal net formed by aluminosilicate-oxygen tetrahedra (^{2}) (Fig. 1a) becomes hexagonal upon heating (Fig. 1b).

Fig. 2. Diagram of the changes occurring in the structure of phlogopite in the plane (001) upon heating

Figure 2: Fig. 2. Diagram of the changes occurring in the structure of phlogopite in the plane (001) upon heating

To prove this, let us consider a fragment of the projection of the phlogopite structure onto the plane (001) (Fig. 2). Solid lines show the Mg octahedron and the silicon-oxygen tetrahedra (ABC) associated with it at room temperature. The angle of rotation φ of a tetrahedron about the vertical axis is determined by the ratio of the dimensions of the octahedron and tetrahedron in the indicated projection (3,4). In phlogopite and biotite this angle is 2–10°, while in muscovite, where the Al octahedron is smaller than the magnesium one, it is 12–15° (3,5,6).

Upon heating, the Mg-octahedron expands and occupies the position indicated by the dashed line. In order to conform to the expanded octahedron, the tetrahedra need only rotate about their heights toward the base, with a simultaneous displacement of the centers from O to O'. At a certain temperature the dimensions of the octahedron will become such that the projection of the height of the tetrahedron onto the base ($O'A'$) exactly coincides with $b/6$ ($\varphi = 0$). From this moment the tetrahedra form a hexagonal network.

This consideration is consistent with the fact that the octahedral layer in micas is determinative and controls the lattice parameters (4, 6), while the tetrahedra tend to occupy such a position that the Si—O—Si bonds of neighboring tetrahedra lie in one plane (7).

As soon as the tetrahedral layer has come into correspondence with the octahedral one, the tetrahedra lose the possibility of rotating. Upon further heating they, forming as it were a "strained, rigid" network, offer additional resistance to thermal expansion, and the coefficient of thermal expansion becomes smaller.

Fig. 2. Diagram of the changes occurring in the structure of phlogopite in the plane (001) upon heating

The calculations carried out confirm the above. Let us adopt the following notation (Fig. 2): $b_0 = 6\,EO$—the lattice parameter at room temperature, $b = 6\,AO$—at the temperature of the phase transition, $r = OA = O'A'$—the radius of the base of the tetrahedron, l—the side of the base of the tetrahedron. Then

$$\cos\varphi = EO/AO = b_0/6r = b_0/2\sqrt{3}l. \tag{1}$$

After rotation of the tetrahedra $r = b/6$, and

$$\cos\varphi = b_0/b. \tag{2}$$

The formulas obtained, (1) and (2), correspond to those given in ([3], [4]), but have been derived more simply. Knowing the coefficient of thermal expansion and the temperature of the phase transition, we shall determine φ for fluorophlogopite. Let us take $b_0 = 9.188$ ([8]), $\bar{\alpha}_b = 12 \cdot 10^{-6}$, and $t = 270^\circ$ (from 20 to 290°) ([1]),

$$b = b_0(1 + \bar{\alpha}_b t) = 9.188(1 + 12 \cdot 270 \cdot 10^{-6}) = 9.218\ldots, \qquad (3)$$

$$\cos\varphi = 9.188/9.218 = 0.9967, \qquad \varphi = 4^\circ 40'.$$

The accuracy of the determination of $\bar{\alpha}_b$ is ±15%, and that of the transition temperature is ±30°; therefore $\varphi = 4^\circ 40' \pm 40'$.

Analysis of formulas (1), (2), (3) and the calculations performed show that at small angles ($\varphi < 10^\circ$) a small error in determining l leads to a significant change in φ. Thus, for $b_0 = 9.188$, at $l = 2.66$, $\varphi = 4^\circ 17'$, while at $l = 2.67$, $\varphi = 6^\circ 35'$. The accuracy of determining b_0 has practically no effect on the value of φ, and errors in determining the coefficient of thermal expansion and the transition temperature affect φ to a considerably lesser degree than errors in determining l. It follows from this that, knowing the coefficient of thermal expansion and the transition temperature, one can determine both φ and l with sufficient accuracy.

Thus, assuming for fluorophlogopite $\varphi = 4^\circ 40'$, $b_0 = 9.188$, we obtain $l = 2.663$. This value should correspond to the average distance

between the oxygens of the bases of the tetrahedra, taking into account the existing Si—Al substitutions.

On the basis of the data obtained, it may be assumed that smaller mean values of the CTE in the (001) plane will be observed in micas with relatively large octahedra and small tetrahedra, where the ratio $r = b/b$ is maintained. Such micas may be those in which the octahedral positions, apart from Mg^{2+}, are occupied by Fe^{2+}, while the tetrahedral positions are completely occupied by Si^{4+}, or by silicon and boron.

As for a break in the course of the CTE along the c axis, it can probably be expected in micas with noticeably flattened octahedra, for example in muscovite, which will be associated with straightening of the octahedra and approximation of their shape to the ideal one.

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