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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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FREE ENERGY OF MICA CRYSTALS

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Attempts to measure the free energy of mica crystals have been undertaken repeatedly (^{1,2}). In the work (^{1}), I. V. Obreimov proposed a method and carried out experimental measurements in air and in vacuum. An analysis of this method, given by one of us in (^{3}), showed that it suffers from substantial shortcomings and cannot yield objective results. Here, a new variant of an optical method for measuring the surface energy of mica crystals, free from the shortcomings of (^{1}), was proposed and tested on mica crystals. In addition, in the previous measurements the complex character of the splitting process was not taken into account; this process is accompanied by electrification of the newly formed surfaces of the crystal ($^{9-12}$) and by capillary condensation of water molecules in the region of splitting.

In the present work, on the basis of a dipole model of a mica crystal (^{5,6}), the free energy of its face (001) has been calculated, and conditions have been realized which made it possible to confirm experimentally the results of the theoretical calculations.

Fig. 1. Dipole model of a mica crystal. μ—packet dipole (18 D), μ_1—polar OH^- group (1.5 D). Dimensions in Å.

As was shown in (^{5,6}), the silico-oxygen packets from which mica crystals are built can, owing to the substitution in them of one quarter of the silicon atoms by aluminum, be represented as a system of dipoles with moment $\mu \simeq 18$ D. A schematic picture of the arrangement of the packet dipoles is shown in Figs. 1 and 2.

Assuming that the free energy is determined mainly by the van der Waals attraction of the packet dipoles and by the repulsion energy of the hydroxyl groups of the packets, we estimate its magnitude as

$$u' = u_1 - u_2 = K n_0 \frac{2\mu^2}{r_0^3} - u_2. \tag{1}$$

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

Here u_2 is the repulsion energy of the OH groups, n_0 is the number of dipoles per 1 cm^2 of cleavage surface, r_0 is the fundamental distance between the centers of the nearest interacting dipoles, equal to 10 Å.

$$K = \sum_i (3\cos^2\alpha_i - 1)\left(\frac{r_0}{r_i}\right)^3 \frac{n_i}{2} = \frac{K' + K''}{2} \tag{2}$$

is a structural coefficient representing a correction factor

to the interaction energy of a pair of dipoles of two neighboring packets—

$$u_0 = \frac{2\mu^2}{r_0^3};$$

α_i is the angle between the line connecting the centers of the dipoles and the direction of their axes; n_i is the number of dipoles at a distance r_i. In formula (2), the interaction of dipoles at distances greater than 12 Å was taken into account. At smaller distances they were treated as point charges, and their energy was referred to u_0.

Fig. 2

Fig. 2. Pattern of dipole nodes of the lattice in the cleavage plane

Fig. 3. Change in the work of peeling a plate from a mica crystal in vacuum $\sim 10^{-1}$ mm Hg as the splitting wedge advances: 1—at $v \simeq 0.05$ mm · s^{-1}, for $h = 38\mu$; 2—at $v = 0.5$ mm · s^{-1}, for $h = 30\mu$. The first point is the work at atmospheric pressure

The coefficient K will be expressed as the sum $K' + K''$. The term K' takes into account the interaction of some dipole of the lower half of the crystal (for example 0_1, Fig. 2) with all dipoles of the upper half. For the interaction of 0_1 with 319 dipoles $K = 6.12$. K'' is the structural coefficient for the interaction of some dipole of the upper half of the crystal with the dipoles of the lower half not included in K'. For 263 dipoles $K'' = 1.53$.

The oxygen atoms of neighboring packets come into contact only through K^+ ions (7), which are rather sparsely distributed between the packets. Therefore the energy of their interaction, associated with London forces (8), is comparatively small, and we do not take it into account. But the attraction of packet dipoles is accompanied by repulsion between the polar groups OH$^-$ and the K^+ ions of neighboring packets.

Fig. 4. Change in the work of splitting with advance of the wedge over time at constant vacuum $6 \cdot 10^{-2}$ mm Hg, artificial ionization of the air, and admission of moist air

Figure 3: Fig. 4. Change in the work of splitting with advance of the wedge over time at constant vacuum $6 \cdot 10^{-2}$ mm Hg, artificial ionization of the air, and admission of moist air

At sufficiently low temperatures, taking into account only the nearest interactions, for the repulsion energy we have

$$u_2 = \frac{n_0}{2}\, e\mu_{\mathrm{OH}} \left(\frac{1}{r_1^2} - \frac{1}{r_2^2}\right). \tag{3}$$

Here $e = 4.8 \cdot 10^{-10}$ esu, $r_1 = 4$ Å, $r_2 = 7.8$ Å (7), $n_0 = 4.3 \cdot 10^{14}\,\mathrm{cm}^{-2}$, $\mu_{\mathrm{OH}} = 1.5D$.

Calculations using the formulas given for the free energy yield

$$\sigma = \frac{u}{2} = -530 + 70 = -460 \text{ erg/cm}^2. \tag{4}$$

Direct determination of the value of G is practically difficult because of electrification of the crystals during splitting in vacuum or dry air and capillary condensation during splitting in moist air.

Fig. 4. Change in the work of splitting with advance of the wedge over time at constant vacuum $6 \cdot 10^{-2}$ mm Hg, artificial ionization of the air, and admission of moist air

Experimental measurement of the free energy of mica crystals was carried out by us in a vacuum of the order of 10^{-1}–10^{2} mm Hg, when electrostatic charges can be neutralized both by surface electrical conductivity and by an electrical discharge in the gas. The specific work was calculated from formula (3)

$$A_0 = \frac{3}{8}\frac{Eh^3y^2}{x^4}, \tag{5}$$

where E and h are the modulus of elasticity and the thickness of the plate, y is the thickness of the splitting wedge, and x is the distance from the wedge to the apex of the cleavage region, determined with a microscope.

From Fig. 3 (curve 1) it is seen that, with continuous advance of the splitting wedge at an average speed of ~ 0.5 mm/sec, the work, owing to the increasing density of charges on the surfaces formed during splitting, rises from the "atmospheric" value, whose magnitude is determined by capillary condensation, to the "vacuum" value. Then, when the potential difference between the separated parts of the crystal reaches the value of the discharge potential in the gas, the work decreases abruptly. At a lower density of surface charges, a gradual decrease in the splitting work is observed owing to dissipation of the charges by the mechanism of surface electrical conductivity (10) (see Fig. 4). Then artificial ionization of the gas in the instrument removes the remaining charges from the surface, and the work decreases abruptly to a value of ~ 960 erg/cm^2, corresponding to the energy of dipole interaction. Admission of moist air into the instrument is accompanied by a gradual increase in the splitting work owing to capillary condensation of water molecules at the apex of the cleavage. With a sharp increase in the vapor pressure of water, a new jump is observed, which we associate with completion of the process of formation of a water capillary wedge in the cleavage.

Thus, these experimental measurements give for the value

the value of the equilibrium work of splitting the crystal is

$$\sigma = \frac{A_0}{2} = 480 \text{ erg/cm}^2. \tag{6}$$

The result obtained agrees well with the energy of dipole interaction of packets in mica crystals calculated above and may be regarded as the free energy of the (001) plane of a mica crystal.

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Note: Figure translations are in progress. See original paper for figures.