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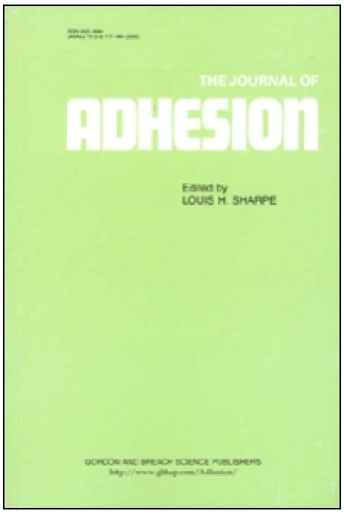

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M. S. Metsik[a]
[a] Department of Solid State Physics, Zhdanov State University, Irkutsk, U.S.S.R.

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Splitting of Mica Crystals and Surface Energy[†]

M. S. METSIK

Department of Solid State Physics, Zhdanov State University, Irkutsk, U.S.S.R.

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The splitting of mica is a complex non-equilibrium process followed by: the stretching of the surface layers till the adhesion forces are broken; the electrification of the surface caused by the non-equilibrium distribution K-ions at the splitting, the gaseous discharge, the emission current between the surfaces; the overcoming of the interaction between the packet dipoles, of the point charges of the electrostatistic mosaic. The principal component of the work of splitting is that of electrostatic interaction of the surfaces being divided. The work is practically equal to the potential energy of the interaction of the crystal packet dipoles and the work of stretching of the surface layers, if the splitting is being endlessly slow or the surface charges are neutralizing. Interaction potential consists of three parts: mutual attraction of packet dipoles ($\mu = 18D$), repulsion of dipole hydroxyl, and repultion of electron shells of oxygen atoms of adjacent packets. The computer calculation of the surface energy value is $\sim$ 300 erg/cm^2. Experimental measurements in vacuum and the neutralization of the charges of the electrostatic mosaic give the value of the surface energy $\sim$ 380 erg/cm^2, that is in agreement with the results of calculations.

Formation of new surfaces in solids is accompanied by secondary processes which make it difficult to measure their surface energy. Such processes are: stretching and breaking of interatomic bonds which is not included in the theoretical calculation of energy; contraction of newly-formed surface layers and corresponding reduction in their potential energy; formation of non-equilibrium electric charges on the surfaces, often leading to electrostatic mosaic structure on the juvenile surfaces and to additional work of elementary

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charge separation, as well as separation of domains of the electrostatic mosaic.

The relaxation of the non-equilibrium state proceeds by emission of electrons, surface charge transfer and gas discharge. To a great extent these processes depend on the rate of separation of the crystal parts. Thus the experimentally measured work of forming new crystal surfaces can never coincide with the theoretically calculated interaction energy of separated parts, but will necessarily exceed it.

This difference increases with the rising contribution of non-equilibrium processes (stretching of surface layers before splitting and secondary electric phenomena).

While the effect of electric phenomena could in principle be made negligible by an infinitely slow process of separating the sample and by carefully neutralizing surface charges, the elastic deformation can not be excluded experimentally and requires theoretical calculation.

After separation, the surface layers of the crystal are compressed by internal forces and form a denser boundary structure. Upon re-contact, these layers may restore their bulk structure only if matching of the surfaces on a molecular level can be ensured for all elements of surface relief. When this can be done, adiabatic cooling should be observed in the contact area because restoration of bulk structure is accompanied by energy absorption.

The present study is devoted to experimental estimation of contribution of irreversible electric phenomena in the measured work of forming new surfaces in mica crystals.

The most suitable method of measuring separation work in splitting crystals is the Obreimoff-Metsik method[1-3]. Figure 1. presents the scheme of the method, which is based on the equilibrium of elastic forces, created by the bent separated part of a crystal, and bonding forces in the split area.

The specific work of separation is calculated as the work of force "F_y" along virtual displacement "dy"[2,3]

$$A_0 = 2\sigma = \frac{d(F_y \cdot dy)}{dx} = \frac{3Eh^3Y^2}{8X^4}\left[1 + \frac{3}{2}\left(\frac{Y}{X}\right)^2 - \frac{9}{4}\left(\frac{Y}{X}\right)^4\right] \quad (1)$$

Here "dy" is found from the equation of elastic curved line:

$$y = \frac{3}{2} \cdot \frac{Y}{X^3} x^2 \left[X - \frac{x}{3} + \frac{3}{2} \cdot \frac{Y^2}{X}\right] \quad (2)$$

and from the expression for equilibrium cleaving force "F_y"

$$F_y = \frac{Ebh^3Y}{4X_3} \quad (3)$$

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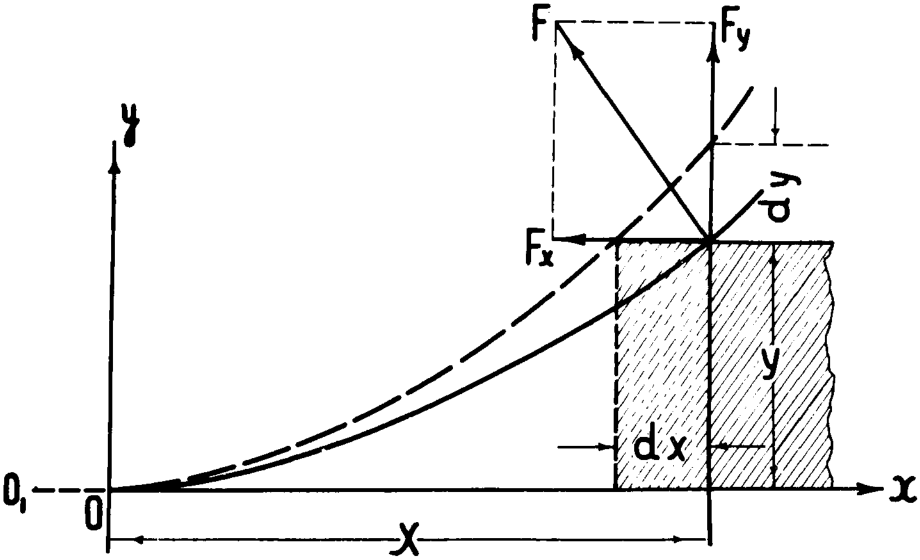

FIGURE 1 Diagram of the cleavage of sheets from the crystal by the Obreimoff-Metsik method.

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where Y is the thickness of the splitting wedge, X is the length of split region, E, h, B are elasticity modulus, thickness and width of the separated crystal plate, respectively; and "x, y" are the coordinates of elastic curved points. (1) can be modified within acceptable accuracy as

$$\sigma = \frac{3}{16} \cdot \frac{Eh^3 Y^2}{X^4}. \tag{4}$$

Gilman's expression, proposed later[4], is a particular case of (1) when (3) is substituted into it.

We used the described method to measure the work of splitting mica crystals in various media.

The results of one of such experiments, carried out in air at pressure of about 10^{-1} mm Hg, are given in Figure 2. It can be seen that as the wedge advances the work increases sharply from its "atmospheric" value to 10–15 × 10^3 erg/cm^2 and then drops.

Experimental data on the formation of an electrostatic mosaic pattern on mica crystal surfaces during the cleavage[2,5] easily explains such behaviour of the work of cleavage on the basis of the electronic theory of adhesion[6]. As new surface elements are formed, the cleavage work increases as a result

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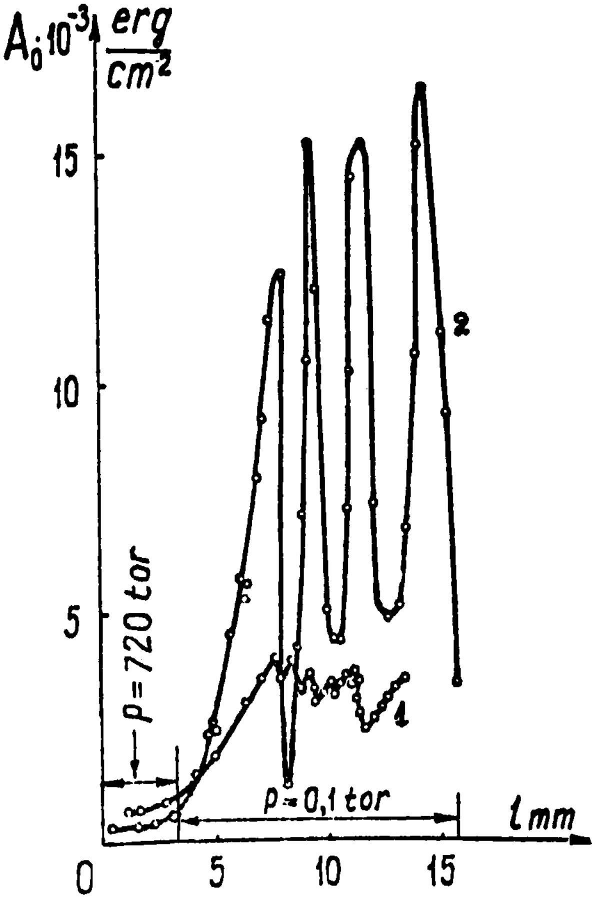

FIGURE 2 Change of work in the cleavage of the mica crystal in a vacuum 10^{-1} mm Hg during the movement of the wedge.
1—at a speed of 0.05 mm sec^{-1}
2—at a speed of 0.5 mm sec^{-1}, sheet thickness 35 mk. First point—work with atmosphere pressure.

of the increase of the mean charge density of the electrostatic mosaic, until the discharge in the rarified gas neutralizes the surface electrostatic mosaic. At this stage the drop is observed.

Figure 3 presents the changes in the splitting work when the wedge is driven in a vacuum of about 0.1 mm Hg. (the work increases as the wedge advances). Then the wedge was stopped, but the mouth of the slit was still advancing and the work was gradually decreasing with time from 12 × 10^3 erg/cm^2 to 1200 erg/cm^2.

By switching on the ionization source and ionizing the residual gas in the experimental cell the work was sharply brought down to the value $2\sigma = 960$ erg/cm^2 due to neutralization of the electrostatic mosaic.

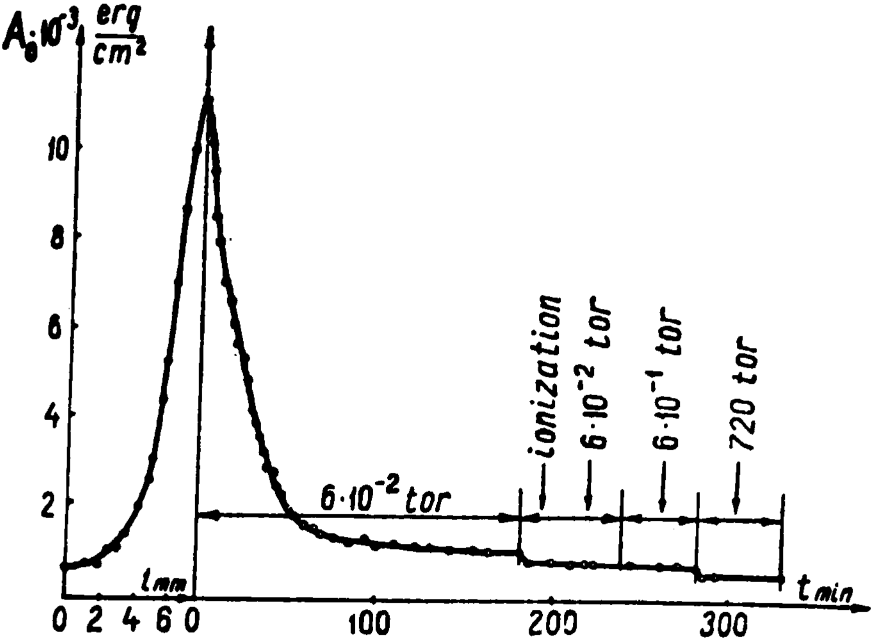

FIGURE 3 Change of cleavage work with wedge movement in vacuum (first part of t); with motionless wedge, ionization and admittance of moist air into cell (second part of t).

Letting the atmospheric air into the cell caused further reduction of work by about 200 erg/cm^2. This reduction is due to partial neutralization of local microscopic activity centers and elementary charges on the surface at the top of the split because of the formation of adsorbed water film, so that

$$2\sigma = 760 \text{ erg/cm}^2.$$

Electric decoration of the crystal surface indicates the existence of residual point centers of electric activity on the surface, which have very large relaxation times. The decoration was carried out by means of charged particles of finely dispersed powder.

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Figure 4 presents a typical electric pattern of a freshly formed surface. Here the lighter spots correspond to charged activity centers. Their surface density is up to ~7 × 10^7 cm^{-2}. Part of these centers survive even after boiling the crystal in water (Figure 4–2).

Let us compare the theoretically calculated free energy with the experimental value of the formation work per unit area of new surface.

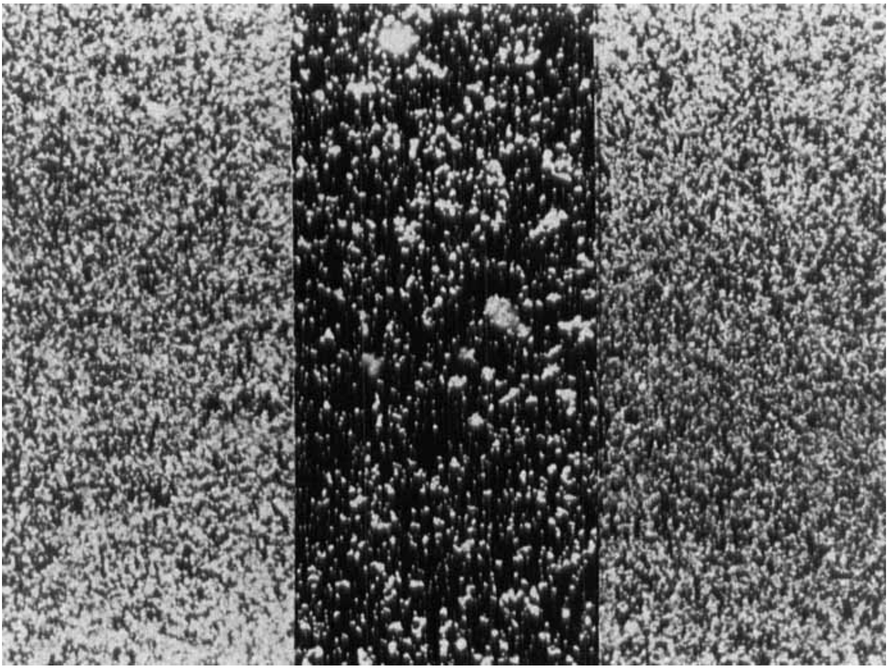

FIGURE 4 Microscopic picture of the decoration of electric activity centers of mica crystal surface (light spots, enlargement 100);
1—new surface, developed in air;
2—surface after boiling in water for 6 minutes
3—after new splitting of boiled crystal.

As was shown in[2,7] mica crystal may be considered as a stack of flat silicon—aluminium-oxygen packages each one approximately 10 Å thick. Within the package the bonds of Si, Al and 0 are mostly covalent, but the net charge of a package is negative due to substitution of one-fourth of tetrahedral Si atoms by Al atoms. We ascribe this negative charge to the oxygen atom (or to hydroxyl) in the octahedral layer of a package. This charge is compensated by that of an interpackage potassium ion.

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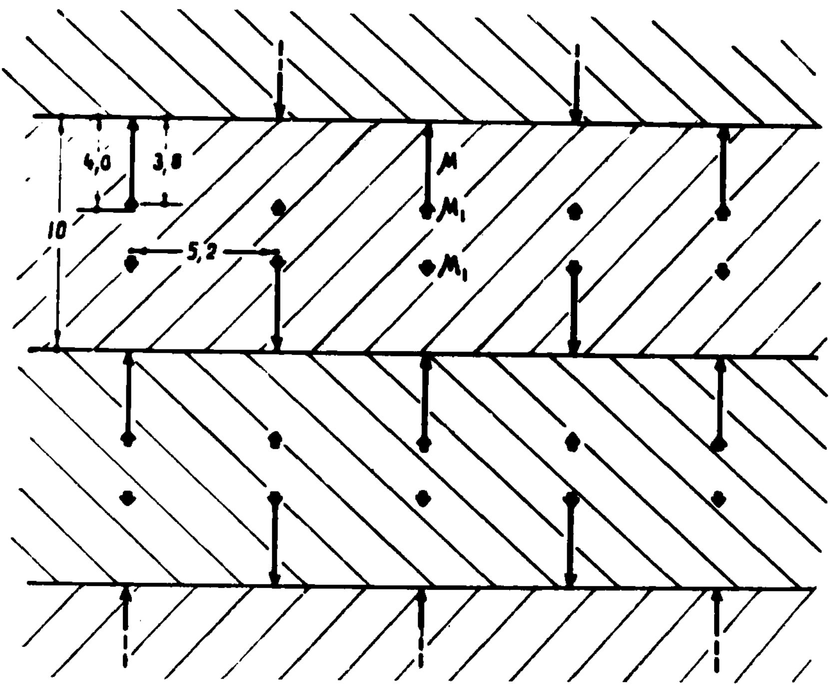

FIGURE 5 Dipole model of mica crystal
μ—packet dipole ($\sim$ 18 D),
μ_1—polar group OH$^-$ ($\sim$ 1.5 D).
Sizes in Å.

The distance between K^+ and 0^- ions is approximately 3.8 Å. These ions form strong package dipoles with the electric momentum $\mu = 18D$.

Thus mica crystal can be represented by a dipole model, given in Figure 5. As the packages themselves are covalent, the package-to-package interaction that has to be overcome in splitting the crystal along a cleavage plane is due to a large extent to ionic-electrostatic attraction of package dipoles.

In this assumption the package interaction potential can be expressed by the following equation:

$$U = \frac{A}{Z_1^3} + B\left(\frac{1}{Z_2^2} + \frac{1}{Z_3^2}\right) + C\exp\left(-\frac{Z_4}{\rho}\right), \tag{5}$$

where

$$A = K_1 n_0 \cdot 2\mu;\ B = K_2 n_0\, e\mu_1;\ n_0 = 4.3 \times 10^{14}\text{cm}^{-2};$$

$$\mu = 18D;\ \mu_1 = 1.5D;\ \text{in Å},\ Z_1 = 10;\ Z_2 = 4;\ Z_3 = 7.8;$$

$$Z_4 = 3{,}4;\ C = 2.10^6\text{erg/cm}^2;\ \rho = 0.31510^{-8}\text{cm}$$

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The Madelung coefficient K_1 was calculated by means of an electronic computer: $K_1 = 2.745$; $K_2 = 1.3$.

The second term of (5) takes into account the repulsive forces between potassium ions and hydroxyl dipoles μ_1.

The third term is the repulsion energy of electron shells of oxygen layers in two adjacent packages.

The value of ρ in (5) was found from the experimental curve of crystal compression $\Delta h/h$ versus pressure P

$$E = Z_1 \frac{dP}{dZ_1}. \tag{6}$$

It was assumed that

$$\frac{\Delta h}{h} = \frac{\Delta Z}{Z},$$

that is the compression, takes place at the expense of interpackage spaces. This assumption is justified by the fact that the macroscopic elasticity modulus of mica crystal is approximately, by an order of magnitude, smaller than that of the packages themselves (4 × 10^3 and 30 × 10^3 kg/mm^2 respectively).

From (5) one can obtain

$$\sigma = 390 - 70 - 20 = 300 \text{ erg/cm}^2. \tag{7}$$

Comparison of the calculated free energy of the cleavage plane (001) with the experimentally determined value (380 erg/cm^2) shows satisfactory agreement of the two, but the measured formation work per unit area is larger than the calculated free energy of the crystallographic plane (001). This is due to our neglecting both the deformation energy of surface layers and interaction energy of charged activity centers, which are generated in the process of splitting and remain on the surfaces for a long time.

Separate evaluation of these factors in further calculations will make it possible to define their contributions into the experimentally measured work of splitting the crystal.

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