INTRODUCTION

It is supposed that one of the factors inducing isomorphic transformations in minerals may be external pulsed mechanical influences on the crystal lattice of minerals appearing owing to earthquakes. Under appropriate conditions, such influences can result in the focusing of energy at an excitation of several areas on the surface of a crystal and stimulate the occurrence of a chemical reaction. This concept is illustrated below by a number of model examples. A method is proposed for the calculation of corresponding effects and their investigation by computer experiments.

PROBLEM FORMULATION

It is known that most minerals are isomorphic mixtures of complex variable composition. Such objects are often classified as solid solutions. Their analogy to normal solution is that some particles penetrate into the area dominated by other particles. This process is readily explained for normal solution on the basis of kinetic models and the classical diffusion theory. Although superficially similar to diffusion in normal solutions, events occurring in solid solution are physically fundamentally different. In normal solutions, diffusion fluxes of particles are controlled by the character of their thermal motion and the occurrence of collisions. In solid solutions, such fluxes are solely related to vibrations of sufficiently large amplitude and must be described in terms of the theory of chemical reactions, in particular, as a result of isomer–isomer conversion and tunneling.

These problems are considered within mechanochemistry, which addresses, in particular, chemical transformations in solids under the influence of shock waves, cavitation in viscous media, and deformations and shear in stressed structures [1, 2]. A number of geochemical phenomena can also be explained on the basis of mechanochemical concepts.

Such phenomena are very slow, and the experimental determination of their kinetic characteristics is generally impracticable. For their efficient investigation, very helpful may be computer experiments based on models adequate to natural systems and appropriate numerical algorithms and computer programs. The modern state of the theory of microprocessors and the advent of supercomputers make the solution of the problem of isomorphic transformations and their development in time quite realistic. The calculated objects can have a very large number of atoms and a complex structure. This paper focuses on this topic.

THEORETICAL BACKGROUND

Let us attempt, first, to answer the question of why a diamond crystal has an extremely high strength and resistance to external mechanical influences. The reader may claim that this has long been explained: the diamond has a perfect crystal structure (perfect shape in terms of construction statics) and strong C–C bonds. The latter statement is questionable. Indeed, the fundamental physical principle of short-range interactions and particular quantum chemical calculations for small diamond clusters have unequivocally demonstrated that the character of C–C bonds in diamond ceases very rapidly to change with increasing cluster size and is controlled mainly by the C–C fragment. This is reflected in the lengths of bonds: the lengths of C–C bonds in diamond and organic molecules are similar and approach $1.5\,\text{Å}$.

Therefore, it can be stated that there is no significant difference between the bond strengths in the nodes of tetramethyl methane, $(\text{CH}_3)_4\text{C}$, and diamond. What, then, is the matter?

Leaving aside for the moment the details of calculations, let us consider as an example the model of the section of a diamond crystal consisting of 182 atoms (Fig. 1). Let an external mechanical force affect one of the surface atoms. The energy of this action will be transmitted into the object as a complex wave motion. The computer analysis of such a motion (Fig. 2) shows that, owing to the homogeneity of the structure, this energy will be distributed over the whole volume. In every particular area,
the concentration of energy will be inversely proportional
to the volume of the object. The destruction of such a
structure requires, therefore, a very strong action on a
very small segment of the boundary, which explains the
tremendous stability of diamond against external
mechanical forces. Already this simple example shows
how a rather interesting conclusion can be drawn using
the most general physical concepts and a computer
experiment.

Before considering further examples, the calculation
scheme should be described.

METHOD OF CALCULATIONS

Without any limitations, atomic vibrations in a solid
can be described within the general theory of molecular
vibrations [3]. It was shown [4] that the displacements of
atoms from equilibrium positions is specified by the equation

\[
\mathbf{r} = \Delta \mathbf{EB} \mathbf{L}_{p} \left( [\delta \sin \nu t] [\delta \nu]^{-1} \mathbf{L}_{p} \mathbf{B} [\mathbf{r}(t = 0)] \right.
\]

\[
+ [\delta \cos \nu t] \mathbf{L}_{p} \mathbf{B} [\mathbf{r}(t = 0)] \right).
\]

where \( \mathbf{r} \) is the column matrix of atom displacements
from the equilibrium positions, \( E \) is the diagonal
matrix of the reciprocal masses of atoms, \( \mathbf{B} \) is the
matrix specifying variations in bond lengths and
valence angles depending on the displacement of atoms

\[
(q = \mathbf{Br} \text{ and } \dot{q} = \mathbf{B}\dot{r}),
\]

are the transformation matrices from the initial coordi-
ates \( \mathbf{L}_{q} \) and momenta \( \mathbf{L}_{p} \) to normal coordinates
and momenta,

\[
(q = \mathbf{L}_{q} \mathbf{Q} \text{ and } p = \mathbf{L}_{p} \mathbf{P}),
\]

\( [\delta \sin \nu t] \) and \( [\delta \cos \nu t] \) are the diagonal matrices with
elements \( \sin \nu t \) and \( \cos \nu t \), where \( \nu \) are the frequen-
cies of the normal vibrations of the object, and \( [\delta \nu] \)
is the diagonal matrix of such frequencies.

As was noted above, all the necessary components can
be determined using the methods described in [3], and
the problem can be solved in any coordinate system with
an arbitrary number of atoms. It is important that the
elasticity of bonds and valence angles necessary for the
computation of the frequencies of normal vibrations can
determine either using modern quantum chemical
calculations or by the method of the solution of inverse
problems for clusters and molecules of the appropriate
structure. The data of infrared spectroscopy can be used
in the latter case. Now consider the results of computer
experiments for some simple models.

Figure 3 corresponds to the model of 17 identical
atoms with the geometry of a polyene-type chain. The
atoms are numbered from left to right. The (1–2) bond is
excited. The (16–17) bond is excited after a time lag, and
its excitation energy is lower by a factor of 10. If one cen-
tral atom is replaced by Ge, the vibration energy of the
same terminal bond will decrease by a factor of 700. The
reason is evident: the heavy atom is weakly displaced, and
almost the whole energy is transmitted in the opposite
direction as a reflected wave. This example is a good illus-
tration of the influence of admixtures and dislocations.

The above examples contained a single excitation
center. Consider now a structure similar to that of 6-sub-
stituted benzene and assume that identical perturbations
occur simultaneously in symmetrical areas at the periph-
ery of the object. Then, the effect of focusing (waves con-
verging toward the center) appears. In such a case, the
energy reaching the central ring is only three times lower
than the total energy of the external excitation. This indi-
cates that, under appropriate conditions, the energy of
external perturbation can be concentrated in some local
zones of the system. This makes possible large-amplitude
vibrations resulting in chemical transformations.