Effect of Breather Existence on Reconstructive Transformations in Mica Muscovite

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Abstract. Reconstructive transformations of layered silicates as mica muscovite take place at much lower temperatures than expected. A possible explanation is the existence of breathers within the potassium layer. Numerical analysis of a model shows the existence of many different types of breathers with different energies and existence ranges which spectrum coincides approximately with a statistical theory for them.

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INTRODUCTION

Some silicates experience reconstructive transformations, which implies the breaking of the bond between silicon and oxygen, a particularly strong one. Therefore, high activation energies and a very slow reaction speed are expected. In the laboratory, temperatures above 1000°C are necessary. In nature, many years are required. However, recent experiments in some layered silicates such as mica muscovite have been performed at temperatures 600°C below the lowest experimental results previously reported [1, 2]. The authors of these articles have performed experiments with layered silicates and, in particular, with mica muscovite, in an aqueous solution with lutetium nitrate during 3 days at 300°C. After that time about 36% of muscovite has been transformed into lutetium disilicate [3]. The lack of explanation from an approach based on conventional Chemical Kinetics suggested the exploration of new hypotheses. Reactions of this type will be referred hereafter as *Low Temperature Reconstructive Transformations* (LTRT).

>From Transition State Theory, a transition state with higher energy than the reactants has to be formed for the reaction to take place. The activation energy E_a is the height of the energy barrier that has to be overcome. The rate of reaction is, therefore, proportional to the number of linear vibration modes or phonons with energy above E_a. This number is proportional to the Boltzmann factor $\exp(-E_a/RT)$, i.e., the fraction of phonons with energy above E_a, bringing about Arrhenius' law:

$$k = A \exp(-E_a/RT), \qquad (1)$$

where k is the reaction rate constant and the pre-exponential factor A is known as the frequency factor.

There is, however a different type of excitations than the phonons, which appears for large amplitudes of vibration where the intrinsic anharmonicity of the atomic bonds can no longer be ignored. They have received considerable attention from the Nonlinear Physics community during the last decade and are known as anharmonic modes, intrinsic localized modes or *discrete breathers*. The mathematical proof of their existence and the methods to obtain them with machine precision in mathematical models has been firmly stablished in Ref. [4]. In this seminal article the authors also suggest that breathers could produce an apparent violation of Arrhenius' law. Breathers are localized, that is, they involve only a few particles or atoms. The conditions for their existence are the anharmonicity of the potentials and that their frequency has to be outside the phonon band. They are called *soft* if their frequency is below the phonon band, which is only possible in systems with an optical phonon band, of *hard* if their frequency lies above the phonon band. Although the subject is still under discussion it seems very unlikely that they can be observed by spectroscopic means due to their localized nature, the small number of them and the basic principles of Physics [5].

We have tried to explore the *breather hypothesis*, that is, that in mica muscovite, there exist breathers, that they have enough energy to overcome the activation energy, and that there are enough of them to influence the reaction speed [3].

THE MODEL

We have considered vibration in the cation layer, where the potassium ions form a rough hexagonal lattice (see

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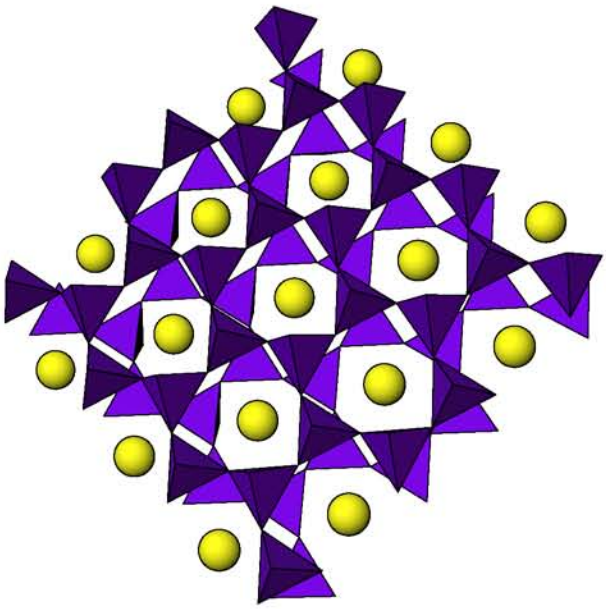

FIGURE 1. Interlayer sheet of the mica muscovite. The circles represent the potassium ions.

Fig. 1). So far, we have only taken into account off-plane vibrations. The model is a classical one with Hamiltonian:

$$H = \sum_{\vec{n}} \left(\frac{1}{2} m \dot{u}_{\vec{n}}^2 + V(u_{\vec{n}}) + \frac{1}{2} \kappa \sum_{\vec{n}' \in NN} (u_{\vec{n}} - u_{\vec{n}'})^2 \right), \quad (2)$$

where $m = 39.1$ amu is the mass of a potassium cation, κ is the elastic constant of the cation-cation bond, $V(u_{\vec{n}})$ is an on–site potential, and the second sum is extended to the nearest-neighbours.The value of the elastic constant κ is taken as 10 ± 1 N/m after Ref. [6].

For the on-site potential, the linear frequency is known after Ref. [7], where a band at 143 cm^{-1} is assigned to the K^+ vibration perpendicular to the K^+-plane in infrared spectra from 30 to 230 cm^{-1}. To obtain more characteristics of the nonlinear potential V, we have performed far infrared spectra above 200 cm^{-1} in CNRS-LADIR [1]. We observe bands at 260, 350 and 420 cm^{-1} as shown in Fig. 2, which we tentatively assign to higher order transitions of the same vibration.

Using standard numerical methods to solve the Schrödinger equation for the K^+ vibrations, with a potential composed of the linear combination with three gaussians and a polynomial of degree six, with adjustable parameters, we have been able to find a suitable potential that fits these bands and their intensities. It is

[1] Laboratoire de Dynamique, Interactions et Réactivité at CNRS-Thiais, Paris

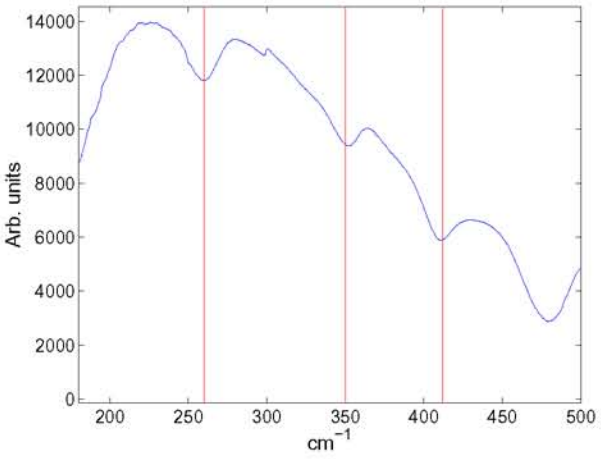

FIGURE 2. Muscovite far infrared spectrum

given by:

$$V(u) = D(1 - \exp(-b^2 u^2)) + \gamma u^6, \quad (3)$$

with $D = 453.11$ cm^{-1}, $b^2 = 36.0023$ $Å^{-2}$ and $\gamma = 49884$ $cm^{-1} Å^{-6}$. To determine the potential, we have also taken into account the limitation to the K^+ displacement due to the muscovite structure.

BREATHERS IN MUSCOVITE

With this model we can obtain breathers with machine precision, using numerical methods based on the anticon-

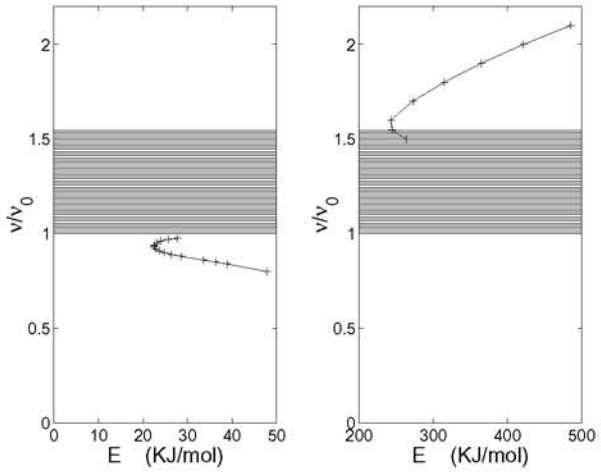

FIGURE 3. Relative frequency versus energy for soft (left) and hard (right) breathers in the muscovite model. Note the different energy scales. The phonon band is also shown. $\nu_0 = 167.5$ $cm^{-1} \simeq 5 \cdot 10^{12}$ Hz.

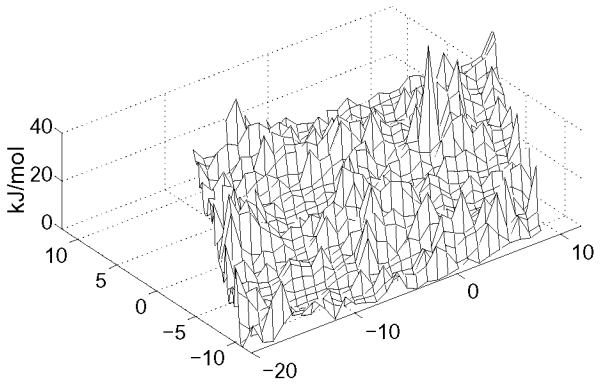

FIGURE 4. Energy density in the thermalized muscovite's model. The units in the x and y axes are in lattice units.

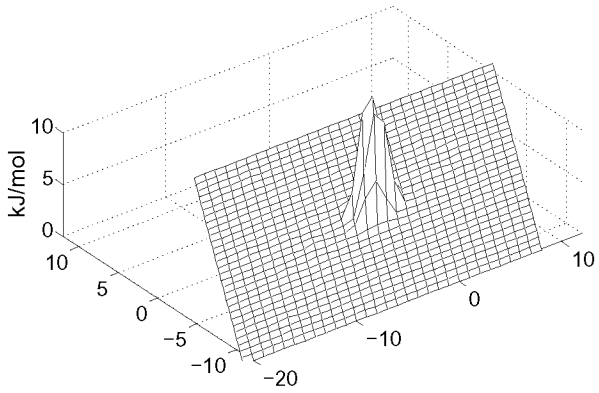

FIGURE 5. Energy density in muscovite's model after cooling. An asymmetric multibreather can be observed. The units in the x and y axes are in lattice units.

tinuous limit. That is, starting with a coupling parameter $\kappa = 0$ and a single excited atom, we obtain the exact solution using the Newton method in the frequency space. By path continuation, we obtain breathers at the physical value of κ.

Due to the characteristic of the potential V, there are both types of breathers, soft and hard ones. They are symmetric and their energies and frequencies can be obtained and are shown in Fig. 3. The expected activation energy for the reconstructive transformation is about 100-200 KJ/mol or higher [8]. Therefore we can see that hard breathers in this model may have enough energy to overcome the energy barrier.

BREATHER STATISTICS

In order to obtain the breather statistics numerically, first we deliver to a system of 50×50 atoms a given energy with random positions and velocities. After some time of evolution the system is thermalized, but it is difficult to distinguish breathers from the subjacent sea of phonons. Second, by adding some dissipation at the borders, the system is cooled, the phonons disappear but the breathers are left in place. We repeat this procedure several hundreds of times, calculate the breather energies and obtain the mean number of breathers and their energy distribution. Fig. 4 shows an example of the distribution of energy density after thermalization, and Fig. 5 shows the resulting breather after the cooling process. The breather energy cannot be taken away by the phonons because its frequency lies outside the phonon band. Among other magnitudes we obtain that the mean number of breathers per site $\langle n_b \rangle$ is around 10^{-3}.

Breathers have different statistics than the phonons as they tend to populate higher energies [9]. In this reference, a theory for breather statistics has been developed. It is based on the following assumptions:

- 2D breathers have a minimum energy Δ. This is an established fact proven in Ref. [10]
- Breathers are created through an activation process, i.e., the creation rate is proportional to $\exp(-E/RT)$
- Large breathers have longer lives than smaller ones as it has been observed in numerical experiments. A destruction rate of the form $1/(E-\Delta)^z$ is proposed, where z is a parameter to be determined.
- At thermal equilibrium, the number of breathers created and destroyed are equal for each energy. That is $\exp(-E/RT) = CP_b(E)/(E-\Delta)^z$, with C a constant independent of the energy and $P_b(E)\,dE$ is the probability of existence (or the mean fraction) of breathers with energy between E and $E+dE$.

With this hypothesis the following magnitudes are obtained:

The mean energy per atom is given by:

$$\langle E \rangle = \Delta + (z+1)\,k_B T\,, \tag{4}$$

with k_B being the Boltzmann constant.

The probability density $P_b(E)$ is:

$$P_b(E) = \frac{\beta^{z+1}}{\Gamma(z+1)}(E-\Delta)^z \exp[-\beta(E-\Delta)]\,, \tag{5}$$

with $\beta = 1/k_B T$.

The cumulative probability $C_b(E)$, i.e., the probability that a breather has energy higher than E, is given by:

$$C_b(E) = \frac{\Gamma(z+1,\beta(E-\Delta))}{\Gamma(z+1)}\,, \tag{6}$$

where $\Gamma(z+1,x) = \int_x^\infty y^z \exp(-y)dy$ is the first incomplete Gamma function.

However, the distribution of breathers obtained numerically cannot be fitted with this theory with the only adjustable parameter being z. This should be obvious by detailed observations of Fig. 5, where it can be seen that the breather is not a single symmetric breather, but a multibreather, i.e., several atoms have similar energies. In other simulations we obtain different multibreathers or single breathers with different symmetries or lack of them. Therefore, there is a *zoo* of breathers, each one of them with a different minimum energy Δ, parameter z and probability of appearance. Moreover, breathers may also have a maximum energy, due to different types of bifurcations. It appears in Fig. 3-left (for the hard breathers on the right hand side, the path has not been continued further, so the maximum energy is not known). Also, if they are or become unstable they will not be observed in numerical simulations or in nature.

Therefore, we have modified the theory, with a maximum energy E_{M}, the previous magnitudes become:

The probability density:

$$P_{\mathrm{b}}(E) = \frac{\beta^{z+1}(E-\Delta)^z \exp[-\beta(E-\Delta)]}{\gamma(z+1,\beta\,(E_{\mathrm{M}}-\Delta))}, \qquad (7)$$

where $\gamma(z+1,x) = \int_0^x y^z \exp(-y)\,\mathrm{d}y$ is the second incomplete gamma function.

The cumulative probability:

$$C_{\mathrm{b}}(E) = 1 - \frac{\gamma(z+1,\beta(E-\Delta))}{\gamma(z+1,\beta(E_{\mathrm{M}}-\Delta))}. \qquad (8)$$

With these modifications we can fit the probability density using six different types of breathers, each one with a different probability of existence P_i. This is, however an approximation, as it is likely that there are many more involved. However, even with several hundreds of simulations it is not possible to obtain a good definition of the numerical $P_{\mathrm{b}}(E)$ and only an approximation for large energies above 100 KJ/mol because the probability of occurrence of each breather with a given energy is very low.

EFFECT ON THE REACTION SPEED

The number of breathers is much smaller than the number of phonons, about one to a thousand, but only the excitations with energy above the activation energy, which is estimated to be $\simeq$100-200 KJ/mol will influence the reaction rate. The increase of the reaction rate with breathers will be roughly equal to the ratio between the number of breathers and the number of phonons above the activation energy, i.e., $\langle n_{\mathrm{b}}\rangle C_{\mathrm{b}}(E)/C_{\mathrm{ph}}(E)$. We estimate it at about $10^4 - 10^5$, in other words, as the three days experimental time leads to about 30% of the transformation performed, the time without breathers to obtain the same result would be $10^4 - 10^5$ times larger and thus, completely unobservable. Furthermore, breather localization will increase the probability of delivering the energy to break a bond, which will increase the reaction rate.

We certainly cannot consider the breather hypothesis as proven, as the statistic theory is only a heuristic one and it is not based on first principles. We also need a theory to obtain the different probabilities of existence of different breathers, and obtain them numerically. We do not know how the energy is delivered and how a quantum treatment would modify our conclusions. At present we are working on these problems. But the fact remains that there is presently no other explanation and that breathers are localized and tend to populate states with higher energy than phonons. Recently, it has been observed that localized vibrations, produced by alpha radiation, travel extremely long distances along the lattice directions, bringing about the sputtering of an atom at the crystal surface [11]. This further reinforces our hypothesis. We can conclude that breathers are good candidates to explain LTRT.

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