Mechanism and intensity of chemical phenomena at the crack tip

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The terminal velocity of a crack determines the reasonability of the application of classical or quantum approaches to the description of phenomena at the crack tip; an expression for the fractoemission intensity of crystals accounting the quantum character of energy transfer at the tip of a fast-moving crack was obtained.

Many investigations into the emission of volatile products (EVP) of chemical processes accompanying fracture and deformation of solids have been reported. The EVP[1–3] or, more generally, fractoemission (FE)[4] implies the emission of neutral and charged atoms and molecules including fractal particles, electrons and photons[5–10] both during the application of mechanical stress to a solid and after completion of deformation or rupture of the solid. FE also explains acoustic, electric and electromagnetic phenomena[11–16] during fracture[17] and deformation[5] of minerals and rocks, which may be impotant for studying earthquakes.[18,19]

Various hypotheses, models and experimental data have been suggested to explain the mechanism and intensity of FE: a local increase in temperature under mechanical effect;[1,7,20–25] tunneling from the initial bonded state into a final unbound state under stress applied to the chemical bond during crack propagation;[26,27] a change in the probability of nonradiative transitions on strong excitation of optical vibrations of the lattice under mechanical effect;[9,12,28] dislocational,[6,8,10,12,29,30] and other mechanisms,[12,31–34] including thermonuclear.[35]

FE is a valuable tool for examining dynamic failure, and it has the potential of providing important information on a number of processes at the crack tip during deformation and fracture of rocks and natural or synthetic single crystals. Of particular interest is the mechanism by which the elastic strain energy at the point of rupture is converted into the excess energy of the two new surfaces formed. Here, we present the conditions for classical and quantum descriptions of processes at the crack tip on cleaving single crystals and obtain an equation for the FE intensity taking into account the quantization of energy in dynamic fracture. There is no doubt that any new concept explaining qualitative and quantitative parameters of FE should take into account both experimental data (emission of gaseous neutral and charged products of decomposition reactions; photons from radiowaves to γ-radiation; elementary particles, *e.g.*, electrons and neutrons) and the theory.

Let us consider the movement of the crack tip, namely, a selected volume in which the rupture and excitation of chemical bonds occur. This volume has the coordinate x, moves at the speed v and has the energy E. The relation between the quantum uncertainties of energy and some quantity x is:

$$\Delta E \Delta x \sim \hbar v \qquad (1)$$

Here, v is the classical rate of x changing. Let τ be a time expressing the rate of change of the coordinate x of the crack tip; then $\Delta E \Delta x \sim \hbar x/\tau$. The coordinate of the tip of a fast-moving crack has a definite value only if its quantum uncertainty is small: $\Delta x << x$, whence $\Delta E >> \hbar/\tau$. The entropy of the system will then have uncertainty:[36]

$$\Delta S >> \hbar/\tau kT \qquad (2)$$

Here, T is the temperature of the system, and k is the Boltzmann constant.

In order to the classical description of the system is to be meaningful, it is necessary for the uncertainty of entropy to be small compared with unity:[36]

$$\tau kT >> \hbar. \qquad (3)$$

Equation (3) allows estimating how essential are quantum effects in dynamic fracture. If the constant $\hbar$ may be considered very small according to the initial conditions of the problem and $\tau kT >> \hbar$, a classical description is sufficient. If the temperature is low, or the value of interest undergoes great changes ($kT << \hbar/\tau$), it is necessary to consider quantum processes in front of a fast-moving crack.

Along with two universal constants, the Planck constant $h = 2\pi\hbar = 6.63\times10^{-27}$ erg s and the Boltsmann constant $k = 1.38\times10^{-16}$ erg K, the equation (3) also contains the values of τ and T. The time of rupture of chemical bonds at the crack tip may be estimated from the equation $\tau = \Delta x/v \approx L/v$, where $\Delta x \approx L \sim 10^{-8}$ cm is a specific distance between the nearest quantum objects (atoms or ions) in the lattice. The theory predicts[37] that a crack should accelerate up to the Rayleigh wave speed; thus, $v \sim 10^5$ cm s^{-1} is the terminal velocity of a crack propagation in brittle materials; it may change within the range $(1.6–5.4)\times10^5$ cm s^{-1} for different single crystals and minerals.[3] Because of this, τ will be determined by the range $(0.6–0.2)\times10^{-13}$ s.

Thus, for maximum-velocity cracks, chemical bonds are traversed by the crack in a time τ comparable to that required for one vibration of the bonds Ω in crystals; that is, $\tau \approx \Omega$. For this reason, there is no possibility of thermal equilibrium being attained. Consequently, 'temperature' can only be defined in terms of the average energy required to break the bonds of molecules decomposed. In such a situation, an 'equivalent temperature' is usually introduced.[1,7] Heating may also occur; however, at the above speed of a crack, the heating front lags behind the crack tip.[24]

Because of the indeterminacy of temperature T, let us estimate how equation (3) is fulfilled for three temperature points:[7] liquid nitrogen (~80 K), room (~300 K) and 1000 K at the above ranges of v and τ changes. The condition of the significance of using equation (3) for the ranges $kT \sim (1–14)\times10^{-14}$ erg and $\tau/\hbar \sim (0.6–0.2)\times10^{14}$ erg^{-1} gives the maximum numerical interval 0.2–9 for $\tau kT/\hbar$. The smaller is this value, the larger is the contribution from quantum effects.

For the major part of single crystals investigated previously,[3] equation (3) is not fulfilled, the contribution from quantum effects is substantial even at high temperatures and provides support for energy quantization in processes that occur on the front of a crack. Moreover, if we admit that the crack delays before the rupture of interatomic bonds for the next time, the real speed of the movement of a 'quantum crack' may exceed the mean velocity of the crack v, determined experimentally. This may lead to indisputable violation of equation (3). The quantum character of the processes at the crack tip explains weak temperature dependence of the FE intensity in mechanochemistry.[7,25]

According to the definition, τ is the time taken for the crack to traverse one interatomic distance; thus, the time within one bond is broken is no longer than $\tau \approx \Omega \sim 10^{-13}$ s, which is close to the periods of Maxwell's atomic vibrations. It is known[38] that as the crack passes through the specimen with the terminal velocity, perfect cleavage surfaces are formed. There is indeed

less time for crack tip–dislocation effects to be involved[39] but crack branching† takes place. If the crack moves through the crystal at a speed lower than some critical value,[41] or stops inside the crystal, various structural distortions and defects are formed at the places where the crack stops and on the cleavage surfaces. Thus, this means that the condition of a quantum character of energy transfer $\tau \approx \Omega$ is favourable for the crack propagation because after each time interval $t = \tau$ the crack moves forward to break the next row of chemical bonds, and its energy does not go inside the crystal but can be consumed only for the movement of the crack itself (recurring energy of broken chemical bonds) and for FE.

On the other hand, excited particles appear at the crack tip as a result of breaking chemical bonds. Let us assume that the relaxation of its excited states occurs by consuming their energy for FE. In the quantitative measurement of FE,[3] its intensity I is determined with respect to the exactly measured cleavage surfaces of a single crystal from which FE occurs. Let $U = n\delta E$ be the total 'potential' energy for FE per unit fracture surface. In case of the violation of (3), for quantum processes at the crack tip energy transfer should occur in portions proportional to $\hbar$:[3]

$$U = n\Delta x\, \delta E/L = n\Delta x\hbar\omega/L. \quad (4)$$

Here, $n \sim L^{-2}$ is the number of quantum objects per unit freshly cleaved surface (exact values of n/L for the investigated crystals are given elsewhere[3]); $\delta E = \hbar\omega$ is the energy brought by each quantum objects into FE, where ω is the cyclic frequency of atomic vibrations.

The approximate equation $\tau \approx \Omega$ can be used to introduce v into equation (4):

$$U \approx hnv/L \quad (5)$$

because $\Delta x = \tau v$ and $\tau \approx \Omega = 2\pi/\omega$. The equation for the intensity of fractoemission I may be obtained[3] by dividing U by energy u necessary for single FE:

$$I = U/u \approx hnv/uL. \quad (6)$$

Precisely the same results can be obtained from a more universal concept. The concept is based on the application of the uncertainty relation to energy (ΔE or H^*) and time (Δt or T^*): $\Delta E\Delta t \geq \hbar$ or $H^*T^* \geq \hbar/2$.[42,43] Results of these works do not impose any restrictions on the applicability of the uncertainty relation to any dynamic process in respect to quantum objects. The chemical bond is an obviously quantum object and the rupture or the rate of rupture of chemical bonds in a crystal by a crack is a dynamic process. It allows us to relate the uncertainty relation to FE *via* velocity $v \sim 10^5$ cm s^{-1} of application under mechanical energy to the solid lattice:[44] the speed of crack tip v_c on fracture,[17,45,46] shear wave velocity in the glide plane (dislocation velocity) v_d[6,47] and/or the rate of deformation twinning v_{tw}[10,48] (other processes under mechanical action on a crystal lattice are the result or a combination of these basic phenomena): $\Delta t = L/v$, where L is a typical linear size of broken or excited chemical bonds and other quantum objects (cores, deeper electronic shells, chemical bonds, point defects, *etc.*) during fracture or deformation of solids in the field of applied mechanical stresses. It follows that indeterminacy in the energy of each single quantum object, which falls into the field of action of mechanical loads, is $\Delta E \geq \hbar/\Delta t = \hbar v/L$. Let us assume that the ΔE of each quantum object is expended on FE. Hence, $U = n\Delta E$ is the total 'potential' energy for FE, where $n \sim L^{-2}$ is the number of formed quantum objects per unit of freshly cleaved surface during fracture or per unit surface of glide plane during deformation or per unit surface of twin boundary during mechanical twinning of crystal. Then for intensity I_i of FE for i type we obtain the expression $U = \sum U_i = \sum I_i u_i = n\Delta E \geq \hbar v n/L$, where U_i is the total energy consumed for i-type FE, and u_i is the energy required for single i-type FE. In conformity with the cleavage of single crystals it follows that the FE intensity of any type cannot be lower than a certain level, as $I_i \geq \hbar v_c n/u_i L$. The concept allows the estimation of the lower limit of FE intensity during cleaving of solids.

Let us analyse the kinetic behaviour of CO_2 emission during the cleavage of calcite single crystals shown in Figure 1. The quantum character of processes explains the weak temperature dependence of FE intensity at cleaving of calcite. Moreover, the kinetic curves of mechanical decomposition of calcite crystals, having different initial temperatures, can be explained as follows: the first peak gives the quantitative contribution in percents of 'quantum' effects, and the second, 'classical' or 'hot spots' processes, late in comparison with a quantum on the front of movement of a main crack. Figure 1 demonstrates that the shape and position of second peaks on kinetic curves $\Delta P(t)$ are dependent on the initial temperature T of a single crystal (the same for the first peaks is not observed). The nature of the occurrence of the second peak can be connected with a classical approach to diffusion–desorption phenomena on the cleaved surfaces:[7] at low T, the rate of diffusion–desorption processes slows down on active freshly cleaved surfaces, and this can cause the broadening of peaks and a shift of the second peak maximum to the region of longer time values; an increase in T in the crystal will cause a reverse effect: the narrowing of peak and shift of the second peak maximum to the region of shorter time values.

The empirical expression for the specific FE intensity I [molecule (atom) cm^{-2}] under fracture by the brittle crack propagating in single crystals is as follows:[3,44]

$$I = Bv_c n/uL. \quad (7)$$

The numerical value of the correlation factor of experimental data on FE intensity from properties of the investigated crystals is equal to $B \approx 10^{-26}$ erg s. Equation (7) differs from equation (6) by the factor B, which is of the same order of magnitude as h.

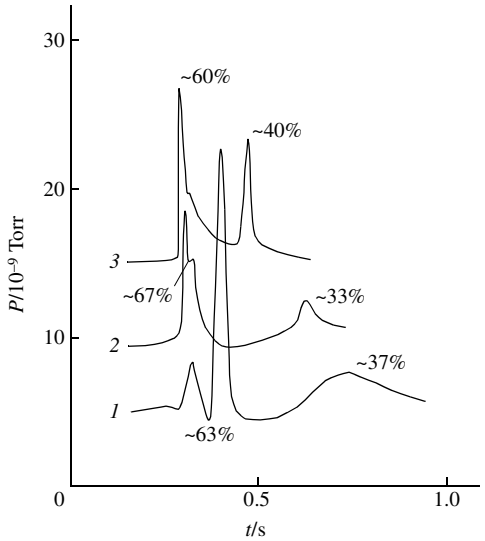

Figure 1 Influence of initial crystal temperature T on the kinetics of $\Delta P(t, CO_2)$ emission (Torr) under the cleavage of synthetic calcite single crystals:[7] (*1*) 77 K, signal amplification factor in arbitrary units is 1; (*2*) 300 K, enhancing of signal is 0.8; (*3*) 415 K, enhancing is 0.5. The time-of-flight mass spectrometry[7,44,49] was used to obtain information on the kinetics and composition of FE during the cleavage and grinding of calcite crystals. During the experiments, a vacuum of 10^{-8}–10^{-10} Torr was used; the sensitivity of the detection system was ~10^{-11} Torr for partial pressure, and it was (1.7±0.1)×10^{11} molecule s^{-1} per 1 mm of the scale of the recording device for gaseous CO_2 flow through the system of leak-in of gases used for calibration of the device. The time constant of the detection of changes in partial pressure for FE from cleaving crystals was ~0.01 s (light-beam oscillograph).

† This phenomenon was specified by a reviewer: '...For isotropic materials (glasses, *etc.*) there are the well-known descriptions of 'mirror', 'mist', 'hackle' and 'branching' which are stages which are passed through by accelerating cracks. In such materials, cracks bifurcate at ~0.5v (where v is the Rayleigh wave velocity...). In crystals with well-defined cleavage planes, the branching is suppressed till higher velocities are reached but it still takes place, see review[40]...'. However, in our opinion, it is very difficult to connect the branching of a crack with the perfection of cleavage surfaces.

The results of calculations according to these equations and all numerical values of the characteristics of crystals and processes necessary for calculation are listed in refs. 3 and 44. The above equations can be applied to estimate the fractoemission intensity of any type.

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