Discussion

Comments on "The question of emission of charged particles in failure of solids"

In the paper by Dickinson *et al.* [1] the results of an investigation of the emission of electrons and ions taking place during the failure of solids are described. These results show that the emissions accompany failure of practically all solids. It is noted that an anomalously intense and long-term emission is observed in cases where the failure of a solid (composite) is accompanied by the breaking of adhesive bonds.

These data are of a fundamental scientific significance, and are original in the aspect of detection of the emission of ions taking place during failure of solids. However, the authors do not cite the papers of the researchers who, as early as the 1950s, had first detected the phenomenon of the high-energy electron emission, taking place either in the breaking of adhesion bonds [2], or during cohesive failure of solids [3]. The results of the investigations of that phenomenon, called mechanoemission, which were carried out in a number of countries, were described later in detail in a monograph [4].

It should be particularly noted that international symposia on mechanoemission and the mechanochemistry of solids are held regularly once every two years in the USSR and the German Democratic Republic. The proceedings of these symposia are published. The IXth Symposium on the mechanoemission and mechanochemistry of solids was held in April 1983 in the German Democratic Republic.

The studies presented on that occasion proved to be unknown to Dickinson *et al.* [1], therefore we will here outline briefly the contents of our studies on mechanoemission.

In 1953, when studying the adhesion of films, it was detected that the tearing off of polymeric films in vacuum is accompanied by the emission of electrons [2]. The emission was observed, not only at the moment of breaking of adhesion bonds, but also after tearing off of the surfaces, at least, from one of them. This process was called postemission. The energy of electrons emitted during the breaking of adhesive bonds amounted to tens of kiloelectronvolts. Under these conditions, the initial (at the moment of breaking of the adhesion bonds) intensity of emission amounted to as high as 10^4 electron sec^{-1} cm^{-2}, and the post-emission from the freshly-formed surfaces continued during tens and hundreds of minutes.

When measuring the energy spectrum of the electrons, it was detected that at any given moment the energy of mechanoelectrons lies within a very narrow range of values changing symbatically in relation to a change in the emission flow intensity and to the surface charge [5]. In this case, as appears in Fig. 1, the energy spectrum grows wider as the energy of electrons decreases. The experimental results show that the intensity of the flow and the energy of the mechanoelectrons are determined only by a surface charge [6]. After breaking of the adhesion bonds, the charge of the surfaces is attributable to the splitting of a double electric layer formed during the contact of two heterogeneous bodies.

In this case, the adhesion joint proves to be equivalent to a charged condenser (capacitor). The drawing apart of the plates of that condenser causes a decrease in its capacity; and when there is no leakage of charge due to electrical conductivity, an increase in the potential difference results [7]. In the open air, this leads to a gas discharge, and in a vacuum, to a breakdown due to the emission of electrons and the secondary ionic emission. Under these circumstances, the main flow of charged particles is closed in a crack, and the external radiation detectors register only an insignificant portion of the total flow. The flux in the crack of an adhesive joint was evaluated by the magnitude of the secondary photon emission resulting from the breaking of electrons in the materials of an adhesion couple (it should be noted that in the case of breaking of adhesion bonds, photon emission was also detected by us for the first time [7]). An indirect evaluation of the electron emission flux density according to the photon emission gives a value of 10^{10} electron sec^{-1} cm^{-2}, i.e. the value which is by 4 to 5 orders of magnitude higher than that registered outside the crack [8].

The theoretical and experimental evaluations give values of up to 10^4 cgse for the density of the double electric layer charges; hence, the

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TABLE I

Solid body to be broken up	Method of breaking up	High energy electron emission flux, (pulses sec^{-1} cm^{-2})
Dielectric crystals		
LiF	Splitting along cleavage planes	10^3
NaCl		10^3
$CaCo_3$		25×10^3
Quartz	Bending	10^4–10^5
Mica:		
muscovite	Splitting up	5×10^3
flogopite		5.7×10^3
Amorphous dielectrics		
Fused quartz	Bending	No emission observed
Alkaline glass		
"Batavian tears" from the alkaline glass	Impact	
Polymeric dielectrics		
Amorphous polystyrene	Bending	10^4
Cellulose	Tension	10–10^3
Three-dimensional glyceroesters	Bending	10–10^3
Gutta-percha	Tension	10^3
Polyethylene		10^3
Polyethylene-terephthalate		10^3
Polyurethane rubber		10^3
Polycaprolactam		10^3
Organic glass (polymethylmethacrylate together with a plasticizer)	Bending	No emission observed
Nitrile rubber	Tension	No emission observed
Rubbers based on the nitrile and the natural rubber		
Glass-fibre reinforced plastic	Tension	10^4
Semiconductors		
Germanium, single crystal	Bending	No emission observed
Silicon, single crystal 1.		
2.	Splitting up	
Conductors		
Aluminium, foil	Tension	No emission observed
Stibium	Splitting up	
Bismuth		
Thermographite	Bending	

intensity of an electric field at the juvenile surface formed during the breaking of adhesion bonds can attain values of about 10^6 V cm^{-1}. The non-uniform distribution of charges over the surface causes the appearance of separate areas, on which both the charge and the field are substantially higher. Moreover, electrons are detected on the freshly formed surfaces of dielectrics, whose work function is less than 1 eV.

In a number of cases, the high field strength and low values of work function enable one to explain the phenomenon of mechanoemission by the field effect [9].

The emission of high-energy electrons taking place during failure of solids, which was first detected in 1954 [3], has also been studied in detail.

Table I gives details of all the materials we have

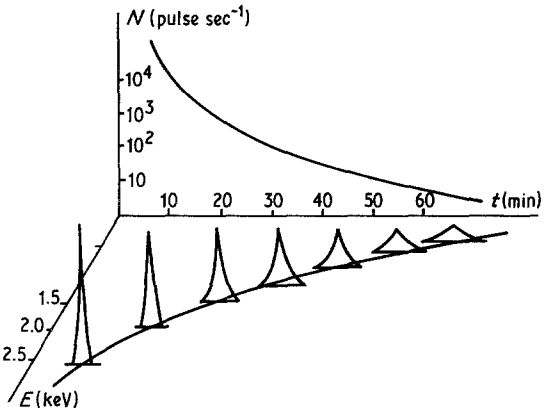

Figure 1 Variation with time of the emission intensity of the electrons characterized by a certain energy.

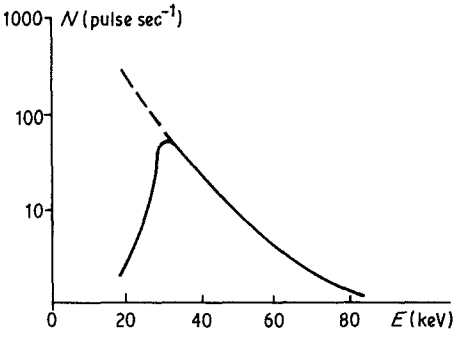

Figure 2 The energy distribution of the electrons emitted during the splitting of a lithium fluoride single crystal.

studied. Under these conditions the inertial detection system was used (having a time constant of about 0.1 sec). Therefore, only a fairly long-term emission could be registered. As appears in Fig. 2, the energy of the electrons observed during failure of materials lies within a wide range of values. However, a considerable part of them possess energy of tens of kiloelectronvolts. The duration of the emission amounted to seconds (and for segnetoelectrics to tens of minutes).

From Table I, it becomes apparent that we have observed long-term emission only during splitting of crystalline bodies. Amorphous bodies, as a rule, do not give any long-time emission of high-energy electrons.

From electrostatics, it is known that the potential in the centre of a charge disc having a radius r, is equal to $V = 2\pi\sigma r$, where σ is the density of a surface charge. Hence, the energy of an electron emitted from the centre of the charged zone is $E = 2\pi\sigma r\epsilon$, i.e. it is proportional to the dimensions of the charged zone.

Thus to obtain high-energy electrons the dimensions of a unipolar-charged emitting surface should be sufficiently large, which is observed only in crystalline bodies. No unipolar-charged zones of large dimension are observed on the juvenile surfaces obtained during failure of amorphous bodies.

At present, the mechanism of emission of electrons cannot be considered to be completely clarified. Apart from the mechanisms considered by Dickinson *et al.* [1], the other mechanisms are also known. For example, the recombination theory of mechanoemission was developed in the paper by Molotsky [10]. In accordance with this theory, electrons are formed as a result of the ionic–electronic emission from the negatively charged wall of a crack during its bombardment by the cations injected by the opposite, positively charged wall. The free cations appear on the opposite wall as a result of the radiationless decay of hot excitons that are generated by impinging mechanoelectrons.

The mechanism of mechanoemission suggested enables one to explain a great many of the phenomena observed during the splitting of single crystals such as quick relaxation of the initial charge of the crack surface, decomposition and the luminescence of crystals during spalling.

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Reply to 'Comments on "On the question of emission of charged particles in the case of failure of solids"'

The first issue raised by Derjaguin and Toporov regards the recognition of their previous work. At the time of writing we were not aware of the work cited. We have since become familiar with the articles accessible to us (which do not include the symposia proceedings mentioned; likewise, their reference [8] does not appear in the appropriate volume of *Sov. Phys. Dokl.*). We have made reference to their work in a number of our publications [1–20] concerning fracto-emission, using their reference [4] because of its wide availability. We quite willingly acknowledge here the importance of their work.

The second issue basically involves a review of the electron emission mechanisms put forth by Derjaguin *et al.* It is clear that fracture-induced electron emission (EE) is a very complicated process. Although Derjaguin *et al.* have outlined a number of observed properties and behaviour of EE from a wide variety of materials it is not clear to us that the mechanism presented is adequate for explaining all EE phenomena in a reasonable fashion. Rather than comment in detail on their mechanism we prefer to summarize an alternative model, aspects of which we have presented previously [17–20]. To date we have restricted this model to fracture of materials where intense charge separation occurs, although it may be possible to extend it to all materials where EE is observed. Our model included many of the concepts Derjaguin and Toporov have presented; however, it differs in several important ways, particularly in terms of the way it relates to the electronic structure of insulator surfaces. In order to provide further support for our model we present here some data both previously published and unpublished. Also, additional results will soon be presented from further studies including quantitative calculations currently in progress. We emphasize that the emission we are discussing is that observed in vacuum (10^{-5} to 10^{-9} Pa), involves charge separation, and concerns primarily the EE observed after fracture (post-or after-emission).

In the case of adhesive failure, the charge separation is particularly intense due to contact charging between the adhesive polymer and dissimilar substrate. Likewise, charge separation in inorganic and organic crystalline materials can be intense and has been attributed to the piezoelectric effect in asymmetric crystals and to defects in the case of symmetric crystals such as alkali halides although the details of the electronic processes yielding this charge separation is, in our opinion, not well understood.

The role of charge separation in the production of EE in vacuum, is not, in our opinion, to induce field emission of electrons. In the case of separation of dissimilar materials as in adhesive failure, the electron states filled above the valence band are still several eV below both the conduction band (or conduction barrier) and the vacuum level [21–23] and are thus unavailable for tunnelling phenomena into the vacuum or for thermally stimulated processes that could lead to emission. There is, to our knowledge, no evidence of sub-eV work functions on fracture surfaces of dielectrics. Furthermore, contrary to Derjaguin and Toporov's conclusions that fracture of amorphous materials do not emit, we have found that a number of non-crystalline materials emit electrons. These include elastomers such as polybutadiene, polyisoprene, polyurethane, and nitrile rubber, inorganic glasses including fused quartz, E-glass, S-glass, and glassy polymers such as polystyrene and PMMA. Furthermore, in the case of unfilled polybutadiene (BR) and polyisoprene [16] the after-emission is quite intense and long-lasting. In addition, if we compare the emission curves for filled (small glass beads) and unfilled BR, where only the former involves extensive charge separation, we see in Fig. 1 (note log scale) that although the emission intensity is considerably higher, the basic shape of the decay curves is the same. It is very difficult to explain EE from the unfilled

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