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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 In order to provide further support for our model we present here some data both previously published and unpublished.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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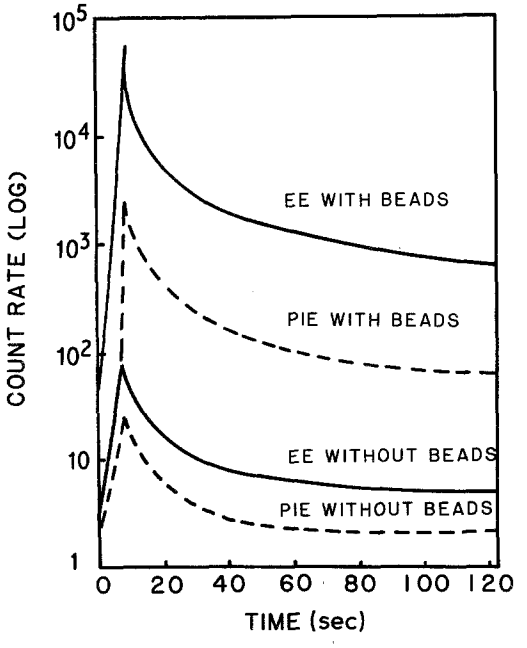

Figure 1 Electron (EE) and positive ion emission (PIE) from the fracture of polybutadiene (BR) both filled and unfilled with small, untreated glass beads.

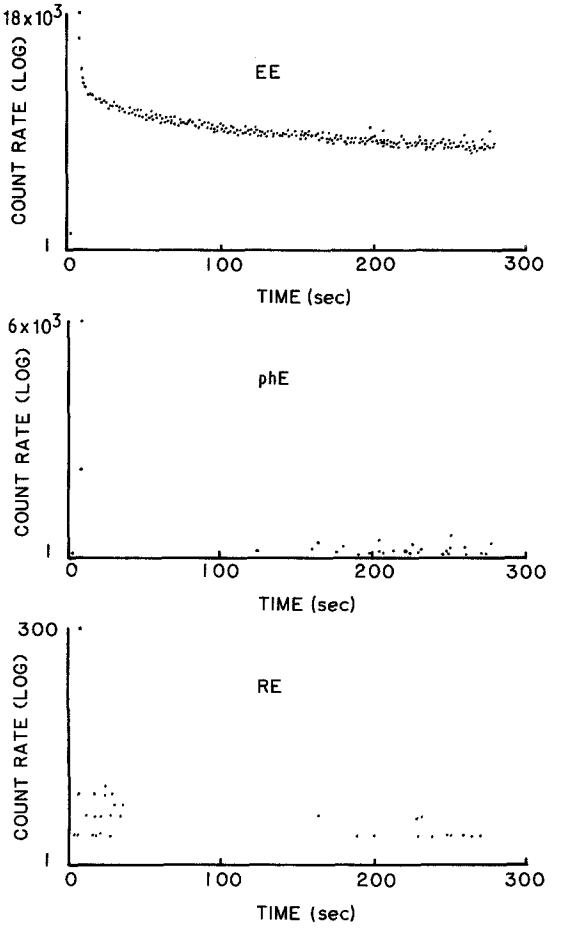

Figure 2 The simultaneous emission of electrons (EE), photons (phE), and radiowaves (RE) from the fracture of polybutadiene (BR) filled with small glass beads.

system in terms of field emission, and yet the similar decay curves suggest a common mechanism.

In our opinion, particularly in the case of extensive charge separation, the high potentials on the fracture surfaces in the presence of gases desorbed into the crack tip yield a gaseous breakdown in the crack. This breakdown produces charged particles (electrons and ions) as discharge products in the crack which immediately bombard the fracture surfaces. It is this particle bombardment of the fracture surface during fracture that we feel is the cause of the necessary surface excitations (e.g. creation of high lying trapped electrons) responsible for the after-emission.

The evidence for the gaseous discharge aligned with fracture in vacuum is the simultaneous emission of visible photons (phE), radio waves (RE), during the rapid rise in electron and positive ion emission during crack propagation. phE, often called triboluminescence, has been observed in a number of materials at higher pressures. Klyuev *et al.* [24] have reported light emission during the peeling of adhesives. Derjaguin *et al.* [25] have observed RE during adhesive failure at higher pressures but imply that at lower pressures (vacuum) it does not occur. With a highly sensitive detector we were able to detect RE during fracture in vacuum and compare the time dependence of RE with the phE and EE. Fig. 2 shows the three types of emission taken simultaneously for BR filled with glass beads, a material for which charged separation is intense, fracture in a vacuum of 10^{-5} Pa. It should be noted that once separation of the two fracture surfaces has occurred (at the peak of the EE) the photons and RE decay essentially instantaneously. Similar results [18] have been obtained on a number of materials including a particulate filled epoxy, fingle cyrstal quartz, polycrystalline PZT, and single crystal sucrose. The RE is evidence of the gaseous discharge occurring during fracture; the phE probably represents photons from both the discharge and the bombardment of the crack walls; the EE during fracture is a combination of electrons escaping the discharge and electrons induced by bombardment. Finally, the EE after

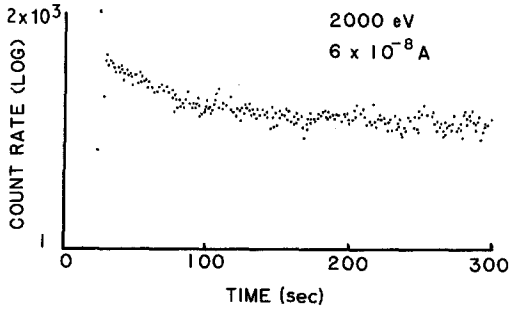

Figure 3 Electron emission from polybutadiene immediately following the bombardment of the surface with 2 keV electrons. The rise to the peak at approximately 20 sec is due to the time for the detector high voltage to reach full value. This decay curve can be superimposed on the EE curve produced by fracture in Fig. 2.

fracture is due to the relaxation of excitations induced by bombardment.

The evidence that electron bombardment alone can produce EE from inorganic crystalline materials is well known and has generally been presented in terms of thermally stimulated electron emission (TSEE) [26]. These studies involve exposure of the material to electrons or other ionizing radiation at low temperature followed by a sweep to higher temperature producing emission peaks similar to thermally stimulated luminescence (TSL) glow curves [27]. Also, following irradiation with electrons and prior to heating, a decaying EE curve is frequently observed at constant temperature, similar to phosphorescence decay [26].

To show that the elastomer BR would yield EE following electron bombardment at room temperature (isothermal emission) we bombarded a thin film of BR for a few minutes with 2 keV electrons at 60 nA. When the electron beam was turned off an electron multiplier viewing the elastomer surface was quickly turned on. The emission curve in Fig. 3 (log scale) shows the resulting emission, with similar decay seen in the fracture-induced EE. On a log scale, the two EE curves of Figs. 2 and 3 can, in fact, be superimposed with excellent agreement. The surface charge density produced by electron bombardment is negligible so that the mechanism for this post-bombardment emission is definitely not field emission but a thermally stimulated process. EE in a polymer would be best explained in terms of the creation of holes and elevated trapped electrons that recombine via radiationless transitions (e.g. Auger recombination) yielding free electrons in the vacuum.

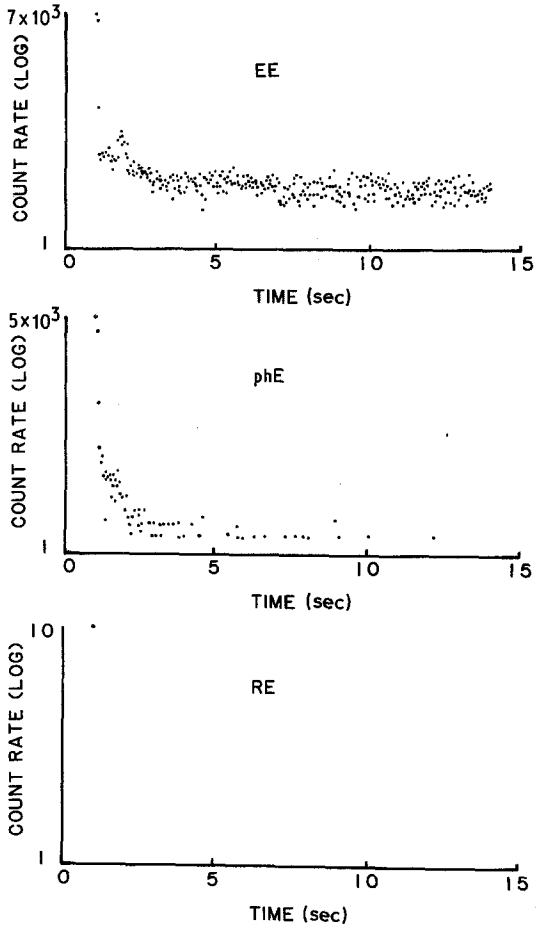

Figure 4 The simultaneous emission of EE, phE, and RE from the fracture of single-crystal SiO_2. Note the after-emission in the photons, long after the fracture is complete. This phE is analogous to phosphorescence following irradiation and is a parallel process to the EE after-emission.

Partridge [28] has suggested that for TSL from a number of polymers the recombination process is not by detrapping but involves the physical approach and reaction of a radical ion R^- (like a trapped electron), and a positive ion M^+ (like a trapped hole) and thus requires long-range motion within the polymer. In this case the parallel EE would again be due to non-radiative decay of excited reaction products.

Electrons released at the surface by such processes in the presence of negative charge patches can obviously yield high electron kinetic energies in the same manner discussed by Derjaguin and Toporov.

It should be noted that we would expect either recombination process mentioned above to be

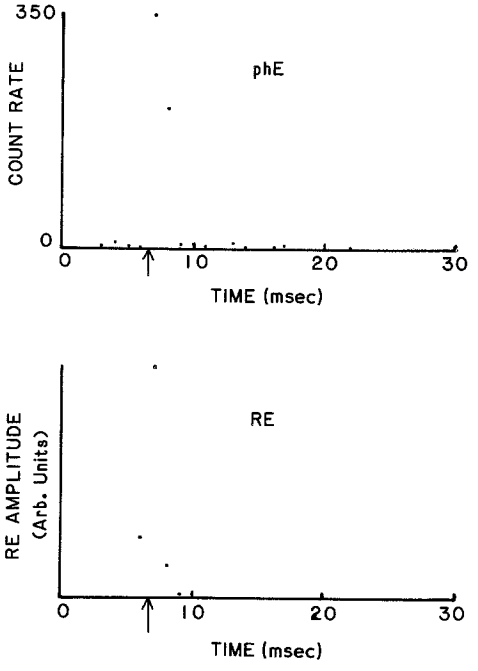

Figure 5 Photon emission and electromagnetic radiation accompanying the fracture of unfilled polybutadiene, where no interfaces are broken, for two separate samples. The two arrows indicate when fracture is occurring as determined by the rise in the accompanying EE. Direct evidence that this latter measurement determines when fracture is occurring is given in [8].

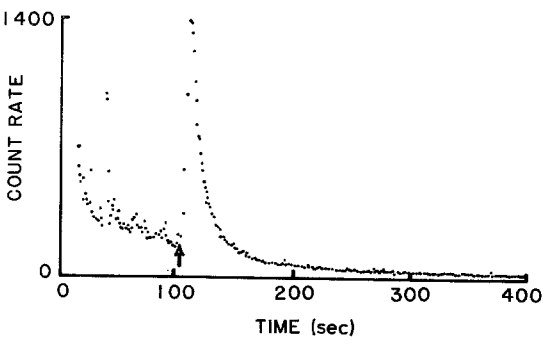

Figure 6 The response of the EE to a small increase (starting at the arrow) in temperature (a thermocouple near the fracture surface registered a 12° C temperature rise) following the fracture of a filled epoxy which showed extensive interfacial failure. Such a response to a programmed temperature increase can be used to test various kinetic models.

accompanied by photon emission (similar to the TSL) and where the luminescence probability is sufficiently high, these photons should be detectable, and we have in fact observed them. Fig. 4 shows this after-emission in the phE for the fracture of single crystal SiO_2 along with the accompanying RE and EE, where a decay curve is clearly seen after fracture which occurs in microseconds. Under favourable positioning of our photon detector relative to the fracture surfaces, we have observed this photon after-emission in the filled BR system also.

Furthermore, the observed similarities of the filled and unfilled BR EE decay curves are quite reasonable in terms of excitation of the polymer surfaces via bombardment by discharge products during fracture; the decay is limited by the thermally stimulated processes leading up to recombination; i.e. release of electrons from traps and motion of charge near the fracture surface, or long-range molecular motion. The great difference in EE intensity for filled as opposed to unfilled BR is due to a much smaller discharge that occurs in the unfilled BR. This discharge can still be detected, however, in the form of much weaker RE (using a more sensitive r.f. pick-up coil) and phE (also less intense). These emissions are shown for BR in Fig. 5 for two different fractures where the arrows indicate the time when fracture was occurring as determined from the charged particle emission. The small breakdown we have detected here for the unfilled BR with the phE and RE indicates that at least on a microscopic level, charge separation is occurring even in an amorphous material.

The details of such charge separation are not clear, although a piezoelectric effect is possible. Wada [29] states that most polymers can exhibit piezoelectricity due to the presence of impurities or imbedded charges in the bulk material. In addition, the fracture process itself, involving the breaking of bonds, may lead to charge separation due to non-adiabatic charge transfer during bond scissions.

Furthermore, in the case of the fracture of molecular crystals (which we discuss in [3, 17, and 19]) the charge densities are generally too low to cause field emission. In addition, there is little possibility of primary (covalent) bond scissions during fracture that might lead to free radical processes. Yet the excitation of the surfaces by particle bombardment (induced by a discharge) would explain easily how EE form materials such as PETN, HMS, and RDX (explosive crystals) and sucrose can be produced. Obvious experimental tests similar to those presented here are suggested.

Further support for the model presented here

can be found in [17–20]. In addition, this model allows us to make a number of predictions, e.g. the photon spectra during compared to after fracture, correlations of intensities of the various fracto-emission. For example, Fig. 6 shows the response of EE from the fracture of a filled epoxy to a small rise in temperature after fracture, the shape of which suggests a non-linear, thermally activated process. We have successfully fit a number of isothermal decay curves to a diffusion-limited rate equation, supportive of a charge transport–recombination process.

Similar predictions can be made and compared with experiments to provide clear tests and establish grounds for accepting, rejecting, or modifying the various proposed models. At this point, we wish to be quite cautious as to the extent of applicability and completeness of the model we have presented, but we note that the results for filled compared to unfilled BR suggest a wide range of application.

Note added in proof: We have recently succeeded in measuring EE decay curves with thermal stimulation, much like Fig. 6, for both filled and unfilled BR. We have fitted these curves with a simple trap model similar to that used for TSL [27]. The same equations and rate constants predict the isothermal EE decay curves such as shown in Figs. 1, 2 and 3.

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