

term on the right-hand side of Eq. (1).

<sup>6</sup>M. Minkowski, *Nachr. Akad. Wiss. Göttingen Math.-Phys. Kl. II.* **1908**, 53, and *Math. Ann.* **68**, 472 (1910).

<sup>7</sup>M. Abraham, *Rend. Circ. Mat. Palermo* **28**, 1 (1909), and **30**, 5 (1910).

<sup>8</sup>P. Penfiled, Jr., and H.A. Haas, *Electrodynamics of Moving Media* (Massachusetts Institute of Technology Press, Cambridge, Mass., 1967).

<sup>9</sup>F.N.H. Robinson, *Phys. Rep.* **16C**, 313 (1975).

<sup>10</sup>V.L. Ginzburg and V.A. Ugarov, *Usp. Fiz. Nauk.*

**118**, 175 (1976) [*Sov. Phys. Usp.* **19**, 94 (1976)].

<sup>11</sup>V.L. Ginzburg, *Theoretical Physics and Astrophysics* (Pergamon, Oxford, 1979).

<sup>12</sup>I. Brevik, *Phys. Rep.* **52**, 133 (1979).

<sup>13</sup>L.D. Landau and E.M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960).

<sup>14</sup>L.P. Pitaevskii, *Zh. Eksp. Teor. Fiz.* **39**, 1450 (1960) [*Sov. Phys. JETP* **12**, 1008 (1961)].

<sup>15</sup>H. Washimi and V.I. Karpman, *Zh. Eksp. Teor. Fiz.* **71**, 1010 (1976) [*Sov. Phys. JETP* **44**, 528 (1976)].

## Linear and Nonlinear Processes in the Erosion of H<sub>2</sub>O Ice by Fast Light Ions

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The erosion of water ice films by fast H and He ions has been found to depend on the electronic energy loss of the ion. At low temperatures the erosion yield is temperature independent and varies quadratically with the electronic stopping power, consistent with a Coulomb repulsion model of ejection. At temperatures above ~100 °K the erosion is found to be temperature dependent and linear with the electronic stopping power. The erosion in this regime can be associated with defect formation and migration in the ice.

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The sputtering coefficients or erosion yields of frozen gases and other nonconducting materials due to irradiation by fast ions have been shown to be considerably larger<sup>1-5</sup> than predicted based on the "standard" sputtering theory, which has been applied so successfully to metals.<sup>6</sup> Whereas sputtering in metals is determined by the energy deposited in elastic nuclear collisions, it has been shown conclusively that the erosion of frozen gases,<sup>1,3,5</sup> alkali halides,<sup>2,4</sup> and certain insulators<sup>7</sup> by fast ions is determined by energy deposited in the material through electronic processes.

Because of the relatively high diffusivity of electrons (for metals) and electrons and holes (for semiconductors), electronic excitation rapidly diffuses from its origin around the track of a fast ion and, by the time it is transformed into atomic motion, it is too dilute to displace atoms of a solid. For insulators this is not the case. The electronic excitation is produced and retained in sufficiently localized states to result in production of point defects in the alkali halides<sup>8</sup> and

ejection of ions from insulating surfaces as observed by electron- and photon-stimulated desorption.<sup>9,10</sup> The excitations can also lead to even more massive atomic displacements as in track formation by energetic ions in insulators<sup>11</sup> and erosion of ice films as in the current experiments.

We have studied the temperature dependence of the erosion of H<sub>2</sub>O ice below 160 °K to determine the mechanisms of erosion produced by electronic processes. A clear temperature dependence has been reported for the ion induced erosion of solid Xe and attributed to a thermal evaporation process.<sup>3</sup> A temperature dependence was also observed in the sputtering of alkali halides by both ions<sup>2,4</sup> and electrons.<sup>12,13</sup> The erosion yield, which increased exponentially with temperature, was interpreted as due to the diffusion of radiation produced color centers to the surface.<sup>2,13</sup> In the present experiments on the erosion of H<sub>2</sub>O ice we find two distinct temperature regions. These depend quite differently on  $dE/dx$ , the electronic energy loss of the fast ions per unit path length,

and are associated with two distinct erosion mechanisms.

The erosion of H<sub>2</sub>O ice films was measured using Rutherford backscattering of 1.5-MeV helium ions and an apparatus described elsewhere.<sup>1</sup> The films are formed by condensation of water vapor at low temperatures (7–80 °K) on a beryllium substrate covered with a 50-Å gold marker layer. Ice formed at these temperatures is amorphous.<sup>14</sup> Scattering from the oxygen atoms of the H<sub>2</sub>O ice film and from the gold marker are clearly observed in the energy spectrum of backscattered helium ions. The total scattering from the oxygen atoms and the shift in the energy of scattering from the gold provide independent measurements of the molecular thickness of the film and hence the erosion yield  $S$ , the number of molecules lost from the film per incident ion. Comparison of the two measurements also provides a measure of the change in the average stoichiometry of the film, which appears to remain close to a 2:1 ratio of hydrogen to oxygen atoms.<sup>1,5</sup>

Measurements of the erosion yield were made for film temperatures between 7 and 155 K. The temperature of the beryllium substrate was controlled by a Cryotip<sup>15</sup> helium transfer tube within  $\pm 0.5$  K during a data run. The experiments were carried out for films between 400 and 2000 Å in thickness; no dependence of the erosion yield on thickness was observed. There was also no beam current dependence for currents less than  $10^{-5}$  A/cm<sup>2</sup>.

At temperatures above  $\sim 130$  °K sublimation competes with erosion at the ion fluxes used in this experiment. The effect due to sublimation, also measured by Rutherford backscattering,<sup>16</sup> has been subtracted from the results for the thickness change under the assumption that sublimation and erosion processes are independent. Ion-eroded and adjacent noneroded regions of the same film were measured sequentially to make this correction. These sublimation contributions never exceeded 30%.

Erosion yields for 1.5-MeV He<sup>+</sup> and 900-keV H<sup>+</sup> are shown in Fig. 1. A definite temperature-independent region is seen in both sets of data, below  $\sim 100$  °K. Such a region has not been reported in the sputtering of condensed xenon<sup>3</sup> or alkali halides.<sup>2,4,12,13</sup> The erosion yields for both ions increase sharply at higher temperatures.

The results of an extensive study of the low-temperature region is shown in Fig. 2. The erosion yield varies approximately as  $(dE/dx)^2$ .

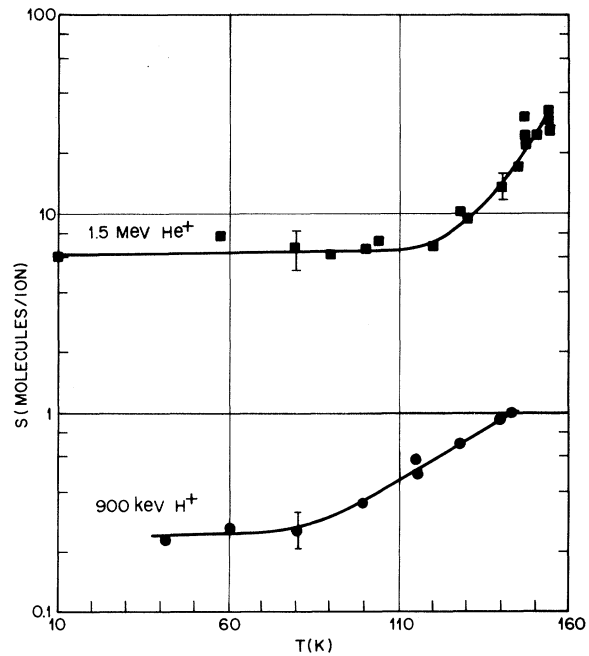


FIG. 1. Temperature dependence of ice erosion yield ( $S$ ) for 1.5-MeV He<sup>+</sup> and 900-keV H<sup>+</sup> ions. The lines are drawn to guide the eye.

The stopping powers used in Fig. 2 are the tabulated equilibrium-charge-state stopping powers.<sup>17</sup> The line in Fig. 2 is drawn through the hydrogen points. The deviations observed for the helium data with respect to this line arise from the non-equilibrium charge state of helium in the thin layer contributing to erosion.<sup>5,18</sup> Calculated corrections are shown for the helium data points<sup>19</sup> which bring them into quite satisfactory agreement with the hydrogen line.

A square-law dependence of erosion on energy deposition implies the sputtering is a cooperative phenomenon which reflects the cylindrical geometry of the ion track. The mechanism could be a cylindrical thermal spike<sup>20</sup> or direct ejection due to Coulomb repulsion,<sup>18,5</sup> both of which yield a quadratic dependence on  $dE/dx$ . We favor the later explanation. The thermal spike requires immediate availability of the deposited energy as heat and a  $\delta$  function in radial width if the model is to yield a  $(dE/dx)^2$  dependence.<sup>20,5</sup> Neither of these conditions applies. On the other hand, the present results are consistent with the conjecture of Haff<sup>18</sup> and Brown *et al.*<sup>1,5</sup> on the existence of a sputtering mechanism based on Coulomb repulsion of ionized species in the track of the incident ion. The  $(dE/dx)^2$  dependence comes directly

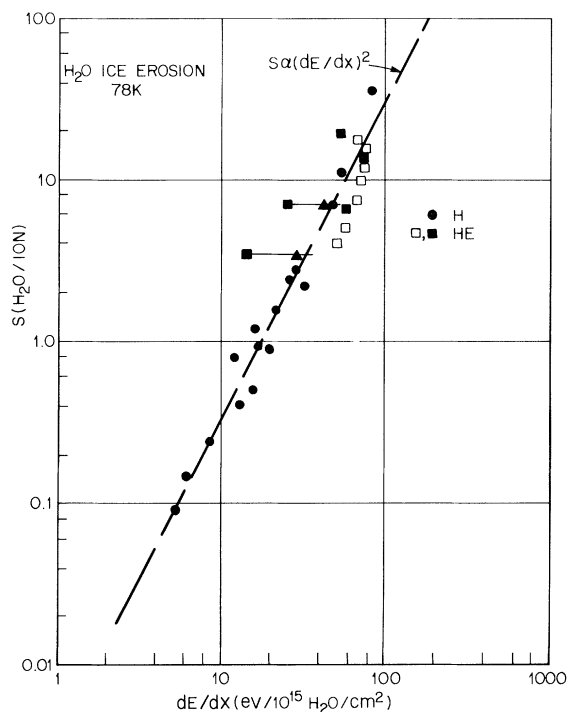


FIG. 2. Erosion yield ( $S$ ) vs electronic energy loss  $dE/dx$  for H and He ions at liquid-nitrogen temperature. The line is drawn through the H ion data (see text). The open He points are from Ref. 3. The horizontal bars on the low  $dE/dx$  He points mark the range of possible charge-state corrections, with the triangles indicating the best estimates.

from this mechanism (cf. Refs. 5 and 19) and the magnitude of  $S$  is obtained with a one-parameter fit of a reasonable mean free path for the repelled ions. Such a model is related to the formation of etchable tracks in insulators.<sup>11</sup> Track formation has been attributed to radial Coulomb repulsion. At a surface, Coulomb repulsion will result in direct molecular ejection and hence film erosion. The molecular charge may be produced by Auger ionization following inner-shell electronic excitation, a process which has been identified in desorption from insulating materials due to incident electrons or uv radiation,<sup>10</sup> or by dynamic charge separation due to passage of the fast ion.<sup>11</sup>

Subtracting the temperature independent portion,  $S_0$ , from each set of data in Fig. 1, the remaining erosion yield scales with  $dE/dx$  and not  $(dE/dx)^2$ . This is indicated in Fig. 3 where the ratios,  $(S - S_0)/(dE/dx)$ , for hydrogen and helium are seen to overlap. The dependence on  $dE/dx$  indicates that electronic energy deposition is still

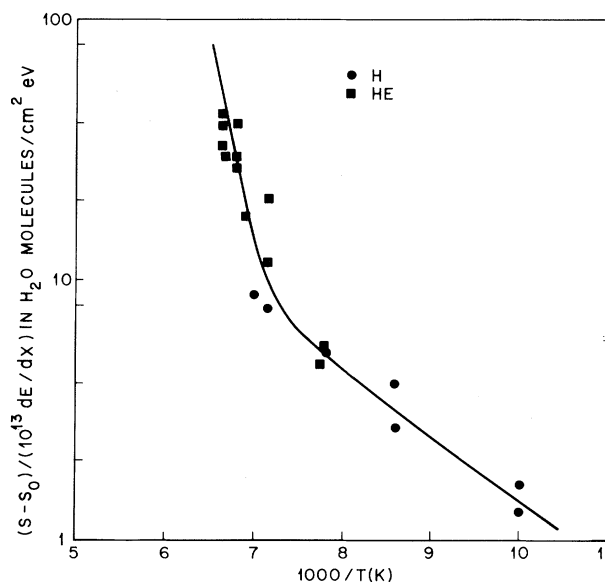


FIG. 3. The temperature dependent part of the erosion yield  $(S - S_0)$  divided by  $10^{13}$  times the stopping power  $dE/dx$ . The curve has a slope varying from 0.05 eV at low temperatures to 0.30 eV at high temperatures.

the source of the erosion, but a different mechanism is operative. The dependence on  $1/T$  is clearly not a simple exponential. The slope of the curve in Fig. 3 corresponds to an activation energy of about 0.05 eV at low temperatures and about 0.30 eV at high temperatures.

The erosion process in the temperature dependent regime is suggestive of radiation chemistry results that show the inactivation of frozen enzymes and the production of radicals in organic compounds by ionizing radiation are temperature dependent above  $\sim 100$  °K.<sup>21</sup> This temperature dependence is related to the diffusion of trapped radical species (e.g., H, OH, solvated electrons) produced by the radiation. In most species studied two activation energies are found,  $\sim 1$  kcal per mole (0.04 eV) and 4–6 kcal per mole (0.16–0.24 eV).<sup>21</sup> The low activation energy is thought to be associated with migrating H and/or OH, but the source of the high activation energies is not clear. The higher activation energies are, however, of the order of magnitude of those found in the temperature dependence of sputtering in alkali halides.<sup>2, 4, 12, 13</sup> As noted, this sputtering has been attributed to the formation and diffusion to the surface of color centers with the subsequent ejection of halides.<sup>2, 13</sup> Color centers also occur in irradiated samples of ice<sup>22</sup> and the activation energy for decay of these species is  $\sim 6$ –9 kcal/

mole (0.24–0.36 eV).<sup>22</sup> It is also noteworthy that the change in slope in Fig. 3 occurs close in temperature to the onset of the amorphous to crystalline transition in ice.<sup>14</sup> Ordering of the lattice may enhance diffusion of dislocated species to the surface, leading to the rapid increase in the erosion yield observed.

The depth in the ice film contributing to the high-temperature erosion can be estimated. With use of a radiation yield of three H<sub>2</sub>O molecules dissociated for 100 eV of energy deposited<sup>23</sup> and associating the erosion yield with dissociation, depths as great as 40 Å may be contributing. Such depths are much larger than those associated with elastic collision sputtering (~5 Å).

The temperature dependence reported for the erosion of Xe films was attributed to a simple thermal spike mechanism.<sup>3</sup> It is, however, possible that those results could alternatively be attributed to diffusion and/or chemical kinetics of, for example, negative molecular ions in a Xe matrix. In any case, a thermal-spike model in H<sub>2</sub>O ice is not very attractive for describing the present results. Such a model cannot describe both the observed temperature dependence and the dependence on  $dE/dx$ .

The measurements reported herein of the dependence of the erosion yields of water ice on temperature demonstrate that at least two erosion mechanisms are operative which have very different dependences on the ion energy deposition. The temperature-independent yield, which has not been found in other systems, is proportional to the square of the electronic energy deposited, and the temperature-dependent yield is proportional to the first power of this quantity. We attribute erosion in the former region to the direct ejection of water molecules through Coulomb repulsion and in the latter region to activated processes controlled by the chemical kinetics of the damaged material in an ice matrix. In addition to the importance of these results for general understanding of the deposition and dispersal of energy in solids following penetration of ion beams, as well as the connections with radiation biology and ion microscopy, these results are of particular significance in astrophysics for studies of the moons and rings of the outer solar-system planets,<sup>24</sup> comets,<sup>25</sup> and interstellar grain surface formation and destruction.<sup>26</sup>

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<sup>1</sup>W. L. Brown, L. J. Lanzerotti, J. M. Poate, and

W. M. Augustyniak, Phys. Rev. Lett. **40**, 1027 (1978).

<sup>2</sup>J. P. Biersak and E. Santner, Nucl. Instrum. Methods **132**, 229 (1976).

<sup>3</sup>J. Bottiger, J. A. Davies, J. L'Ecuyer, H. K. Haugen, N. Matsunami, and R. Ollerhead, to be published.

<sup>4</sup>M. Szymonski, H. Overeijnder, and A. E. DeVries, Radiat. Eff. **36**, 189 (1978).

<sup>5</sup>W. L. Brown, W. M. Augustyniak, E. Brody, B. Cooper, L. J. Lanzerotti, A. Ramirez, R. Evatt, and R. E. Johnson, Nucl. Instrum. Methods **170**, 321 (1980).

<sup>6</sup>P. Sigmund, Phys. Rev. **184**, 383 (1969).

<sup>7</sup>J. E. Griffith, R. A. Weller, and T. A. Tombrello, Bull. Am. Phys. Soc. **24**, 662 (1979).

<sup>8</sup>E. Sonder and W. A. Sibley, in *Point Defects in Solids*, edited by J. W. Crawford and L. M. Slifkin (Plenum, New York, 1972), Vol. 1, p. 201 ff.

<sup>9</sup>T. E. Madey, Surf. Sci. **33**, 355 (1972).

<sup>10</sup>M. L. Knotek and P. J. Feibelman, Phys. Rev. Lett. **40**, 964 (1978); M. L. Knotek, V. O. Jones, and V. Rehn, Phys. Rev. Lett. **43**, 300 (1979).

<sup>11</sup>R. L. Fleischer, P. B. Price, and R. M. Walker, *Nuclear Tracks in Solids* (Univ. of California Press, Berkeley, Calif., 1975).

<sup>12</sup>H. Overeijnder, M. Szymonski, A. Haring, and A. E. DeVries, Radiat. Eff. **36**, 63 (1978).

<sup>13</sup>Y. D. Jammal and P. D. Townsend, J. Phys. C **6**, 955 (1973).

<sup>14</sup>P. V. Hobbs, *Ice Physics* (Clarendon Press, Oxford, 1974).

<sup>15</sup>Cryotip Transfer Systems are products of Air Products, Inc., Allentown, Pa.

<sup>16</sup>W. L. Brown and E. J. Brody, private communication.

<sup>17</sup>H. H. Anderson and J. F. Ziegler, *Hydrogen: Stopping Powers and Ranges in all Elements* (Pergamon, New York, 1977); J. F. Ziegler, *Helium: Stopping Powers and Ranges in All Elemental Matter* (Pergamon, New York, 1977).

<sup>18</sup>P. K. Haff, Appl. Phys. Lett. **29**, 473 (1976); J. O. Stiegler and T. S. Noggle, J. Appl. Phys. **33**, 1894 (1962).

<sup>19</sup>R. Evatt, M. S. thesis, University of Virginia, Charlottesville, Va., 1980 (unpublished).

<sup>20</sup>G. H. Vineyard, Radiat. Eff. **29**, 245 (1976).

<sup>21</sup>See, for example, H. Dertinger and H. Jung, *Molecular Radiation Biology* (Springer-Verlag, Heidelberg, 1970).

<sup>22</sup>J. J. Weiss, in *Physics of Ice*, edited by N. Riehl, B. Bullemer, and H. Englehardt (Plenum, New York, 1969), p. 195; K. Eiben, *ibid.*, p. 184.

<sup>23</sup>See, for example, A. Kupperman, in *Physical Mechanisms in Radiation Biology*, edited by R. D. Cooper and R. W. Wood (National Technical Information Center, Oak Ridge, Tenn., 1974).

<sup>24</sup>L. J. Lanzerotti, W. L. Brown, J. M. Poate, and W. M. Augustyniak, Nature (London) **272**, 431 (1978), and Geophys. Res. Lett. **5**, 155 (1978); A. F. Cheng and L. J. Lanzerotti, J. Geophys. Res. **83**, 2597 (1978).

<sup>25</sup>e.g., F. L. Whipple, in *Comets, Asteroids, Meteorites*, edited by A. H. Delsemme (Univ. Toledo Press, Ohio, 1977), p. 25.