Chemical Effectiveness of Elastic and Inelastic Energy Loss of He^+, Ar^+, and Xe^+ Ions Bombarding Solid Potassium Nitrate†

Shin-ichi OHNO,* Katsutoshi FURUKAWA, and Takeshi SOGA
Department of Chemistry, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-11

(Received December 5, 1985)

Decomposition of crystalline potassium nitrate due to He^+-, Ar^+-, and Xe^+-ion bombardment was studied in the energy range from 20 to 100 keV. The cross sections for producing nitrite ions were for the first time determined to be $5.7\times10^{-20}\,m^2$, $12.6\times10^{-20}\,m^2$, and $22.0\times10^{-20}\,m^2$ for 100 keV He^+, Ar^+, and Xe^+ ion, respectively. Comparing the values of these cross sections with the rate of an elastic and inelastic energy loss of these incident ions, which were calculated on the basis of the theory of Lindhard et al., it may be concluded that inelastic energy is about five times more efficient than elastic energy for the decomposition of the solid potassium nitrate.

Energetic particles lose energy in traversing matter because of two different processes:[2,3]

a) elastic collisions leading to atomic displacements, which are called "nuclear stopping" of the matter for the incident particle,

b) inelastic collisions leading to electronic excitations (ionizations and charge-exchange processes included), which are called "electronic stopping" of the matter. Both "nuclear" and "electronic" collisions may initiate chemical reactions in the material.[1,2,4]

Decomposition of potassium nitrate via electronic excitations has been studied in many works[1,5—12] using α-rays,[7] γ-rays,[5,8—10] or electron beams.[6,12] The only end-products reported are the nitrite ion and molecular oxygen, the initial process being the dissociation of an N–O bond:[7—9]

$$NO_3^- \longrightarrow NO_2^- + O. \qquad (1)$$

On the other hand, elastic collisions are frequent phenomena at relatively low impact energies (≈keV region).[2,3] The energy transferred from incident ions to atomic constituents is so high compared to the binding energy for a molecular and crystalline structure that a chemical reaction may take place in the solid. Thus, Logan and Moore interpreted their results on the decomposition of potassium nitrate by incident 2 keV D^+ and He^+ as due to the atomic displacements.[11]

The present authors reported in a previous communication[1] that potassium nitrate decomposed during bombardment with 100 keV ions generated from discharge of deuterium, helium, nitrogen, and oxygen. The observed results suggested that the reaction proceeded mainly via electronic excitations.

The purpose of the present paper is to clarify the relative importance of electronic and atomic displacement excitations in chemical reactions in potassium nitrate. We aim at obtaining cross sections of the each ion decomposing potassium nitrate which should be determined from the yield-dose curve for He^+-, Ar^+-, and Xe^+-ion bombardment. These noble gas ions transfer their kinetic energy to KNO_3 without themselves taking part in chemical reaction. (cf. H_2^+ or O_2^+; see Ref. 1). The second step to our end is to know the relative amount of energy going into elastic and inelastic processes. We obtain this information from the calculation of stopping power according to the theory of Lindhard, Scharff and Schiφtt.[13,14]

By comparing the cross sections for the reaction with the electronic and nuclear stopping power thus obtained, one may determine the relative effectiveness of elastic and inelastic energy losses of the energetic particles bombarding solid potassium nitrate. Potassium nitrate was chosen because its radiolytic behavior toward ionizing radiations was well known; The only radiolytic products reported are nitrite ions and molecular oxygen.[10,11]

Experimental

Experimental method was the same as that reported previously.[1] Energetic ions were produced by discharge of He, Ar, and Xe in a radio-frequency source,[16] and accelerated at desired energies and were focussed through an aperture (8 mmφ) onto the sample.

The sample was a pressed disk of polycrystalline potassium nitrate. Irradiations were carried out at room temperature in vacuum (ca. 10^{-5} Pa). The current density was 10 μA cm^{-2}. After irradiations, the samples were dissolved in water and the concentration of nitrite ions produced was determined spectrophotometrically[17] by adding 1-naphthylamine and sulfanilic acid.

Results and Discussion

Yield-Dose Curve for the He^+-, Ar^+-, and Xe^+-Ion Bombardment. The amounts of nitrite ion as a function of the incident ion dose are shown in Figs. 1, 2, and 3 for the bombardment of He^+, Ar^+, and Xe^+ ion, respectively. As is seen from the figures, the yields depend on both the mass and energy of the bombarding ions. The rapid initial decomposition is followed by a decline in rate in all the cases examined.

We may assume here that each yield-dose curve includes of two regions: An initial decomposition the rate of which is linear with dose and a final plateau

---

† Chemical Reactions Induced by Energetic Particles. III.[1]

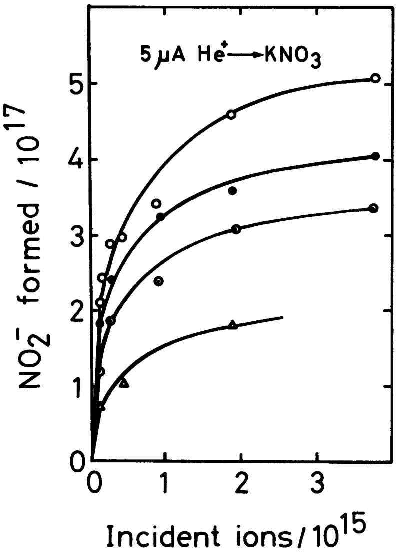

Fig. 1. Nitrite ion formation in potassium nitrate as a function of the energy of incident He$^+$ ions. Ion energy: (△) 20 keV, (⊙) 50 keV, (●) 80 keV, and (○) 100 keV; Ion beam intensity: 6.25×10^{13} ions cm^{-2} s^{-1}.

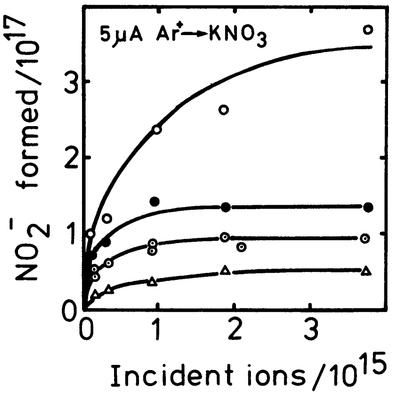

Fig. 2. Nitrite ion formation in potassium nitrate as a function of incident Ar$^+$ ion. Ion energy: (△) 20 keV, (⊙) 50 keV, (●) 80 keV, and (○) 100 keV; Ion beam intencity: 6.25×10^{13} ions cm^{-2} s^{-1}.

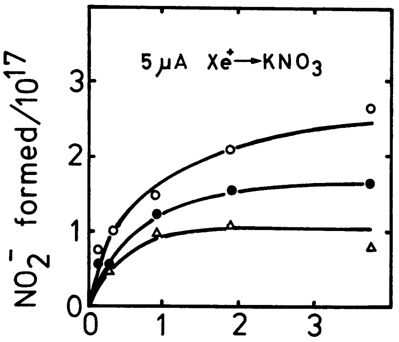

Fig. 3. Nitrite ion formation in potassium nitrate as a function of incident Xe$^+$ ions. Ion energy: (△) 50 keV, (●) 80 keV, and (○) 100 keV; Ion beam intensity: 6.25×10^{13} ions cm^{-2} s^{-1}.

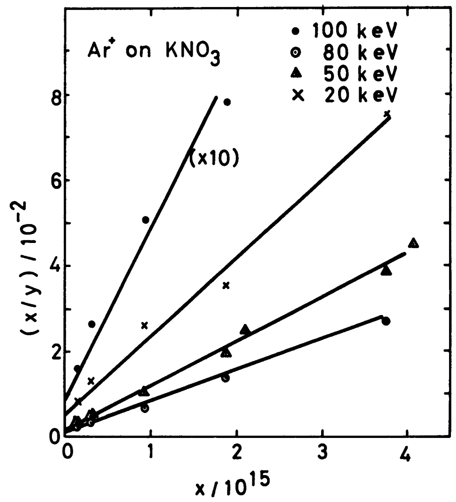

Fig. 4. Plots of x/y vs. x for 20 (×), 50 (△), 80 (⊙), and 100 (●) keV Ar$^+$ ions, where x and y are the number of incident ions and nitrite ions formed, respectively.

region which would be obtained at high doses. If we represent these relation as $y=ax$ and $y=b$, respectively, where y is the amount (=number) of nitrite ion and x is the dose (=number) with a and b being constants, we may obtain an expression:

$$\frac{x}{y}=\frac{1}{a}+\frac{1}{b}\cdot x. \qquad (2)$$

The experimental points in Figs. 1—3 were replotted according to Eq. 2 (See Fig. 4, as an example) to obtain values of a and b for each yield-dose curve. Thus, an initial rate of NO_2^- formation, $Y=(\mathrm{d}y/\mathrm{d}x)_{x=0}$, and a "saturation yield," $(y)_{x=\infty}$, were calculated respectively from the values of a and b above obtained for incident He$^+$, Ar$^+$, and Xe$^+$ ions at an energy of T. The results are included in Fig. 5 and in Table 1, respectively.

The "saturation yields" shown in Table 1 probably represent a steady state between decomposition of NO_3^- to give NO_2^- (Reaction 1) and disappearence of NO_2^- either via a reverse reaction (Reaction 3) or via a further decomposition by incoming ions (Reaction 4):[†]

$$NO_2^- + 1/2O_2(O, O^+, O^-, O_2^-, \text{or } O_3) \longrightarrow NO_3^-, \qquad (3)$$

$$NO_2^- \longrightarrow NO^- + O\ (\text{or } NO + O^-). \qquad (4)$$

Oxygen-containing species in Reaction 3 may diffuse away from the reaction zone; This prevents the re-formation reaction of nitrate ion. Thus, analyses of the "saturation yield" seem very complex; we will hereafter strict our discussion on the initial rate of NO_2^- formation.

Calculation of the Stopping Power. The total stopping power, S_t, can be divided into two parts: $S_t = S_e + S_n$ where S_e and S_n are the electronic and nuclear

---

[†] In 1.4 keV electron-beam irradiation, there is no indication for futrher decomposition of the nitrite ion formed (Ref. 12).

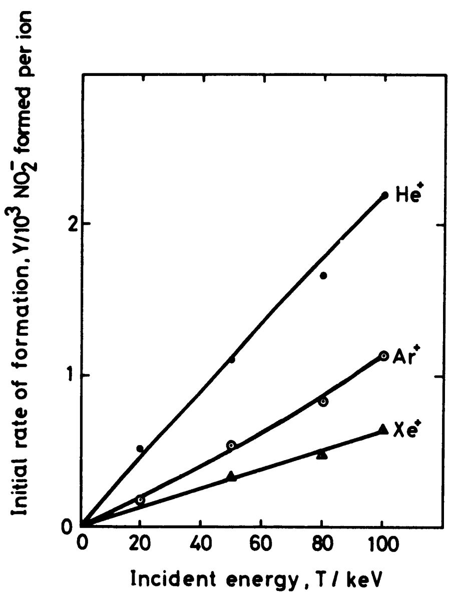

Fig. 5. The initial rate of formation of NO_2^-, $Y=(dy/dx)_{x=0}$, as a function of the incident ion energy, T, for He^+, Ar^+, and Xe^+ ions bombarding potassium nitrate.

Table 1. Saturation Yield (=b)/10^{17} NO_2^- for He^+, Ar^+, and Xe^+ Ions Incident on Potassium Nitrate at Various Energies

Ion energy/keV	20	50	80	100
He^+	2.1	3.7	4.3	5.5
Ar^+	0.56	0.96	1.45	4.0
Xe^+	—	1.46	1.9	3.0

stopping powers, respectively, as discussed in the introduction of this paper.

The electronic stopping power for a particle moving at the velocity v was calculated according to the theory of Lindhard, Scharff, and Schiϕtt:[13,15]

$$S_e = 8\pi e^2 N a_0 Z_1^{7/6} Z_2 (Z_1^{2/3}+Z_2^{2/3})^{-3/2} v/v_0 \tag{5}$$

where a_0 is the Bohr radius of the hydrogen atom; v_0 is the Bohr velocity; Z_1 and Z_2 are the atomic number of the projectile and the target, respectively; N is the atom density of the target material.

The nuclear stopping power was calculated using[14,15]

$$S_n = s_n(8.462 Z_1 Z_2 M_1)/[(M_1+M_2)(Z_1^{2/3}+Z_2^{2/3})^{1/2}] \tag{6}$$

and

$$s_n = 0.5 \ln(1+\varepsilon)/(\varepsilon + 0.107^{0.375}) \tag{7}$$

Here, ε is the reduced energy of the ion and is defined as:

$$\varepsilon = 32.53 M_2 E/[Z_1 Z_2 (M_1+M_2)(Z_1^{2/3}+Z_2^{2/3})^{1/2}], \tag{8}$$

where the ion energy, E, is in keV; M_1 and M_2 are the ion and target masses in amu, respectively.

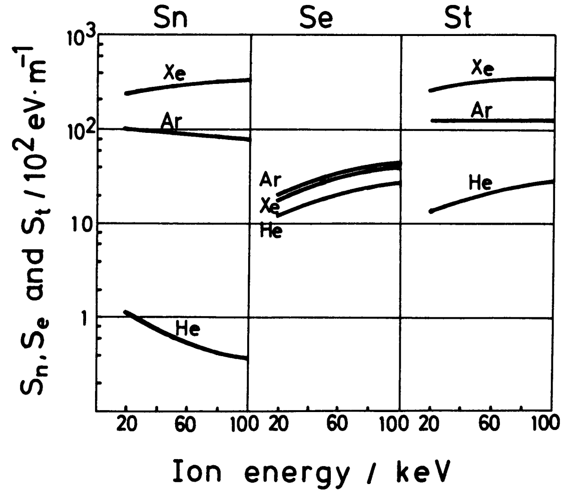

Fig. 6. The stopping powers of potassium nitrate (KNO_3: $10^{23}\,m^{-3}$) for He^+, Ar^+, and Xe^+ ions in the energy range from 20 to 100 keV.
S_n: Nuclear stopping, S_e: Electronic stopping, S_t: Total stopping, $S_t=S_n+S_e$.

For the stopping power of compounds, e.g., KNO_3, the stopping powers of the constitutional element (i.e., K, N, and O) were weighted by their relative abundance; this is called Bragg's Rule. The results of the calculation are shown in Fig. 6, where the electronic, nuclear and total stopping powers in eV m^{-1} of potassium nitrate ($N=10^{23}\,m^{-3}$) for He^+, Ar^+, and Xe^+ ions in the energy range 20—100 keV are plotted. We notice from Fig. 6 that He^+ ion in the energy range 20—100 keV dissipates most of their energy into electronic excitations, while Xe^+ ion in the same energy range into atomic displacement collisions.

Determining the Cross Sections for the Reaction Induced by Energetic Ions. The cross section for reaction of an energetic particle with a molecule in the solid is a function of the kinetic energy of the particle. The initial rate of NO_2^- formation, $Y=(dy/dx)_{x=0}$, for the incident energy at T_0, that is the number of the product formed per incident ion, is expressed as follows:

$$Y = N\int_0^{T_0} Q(T)\,ds \tag{9}$$

Here, N is the number density of KNO_3 in the medium, $Q(T)$ is the cross section that the product, NO_2^-, will be formed in a collision with the particle of the kinetic energy T, and ds is the distance traversed by the particle while in the energy range between $T+dT$ and T. In the continuous slowing-down approximation,[18] ds may be replaced by $dT/S(T)$, $S(T)$ being the total stopping power:

$$Y = N\int_0^{T_0} \frac{Q(T)}{S(T)}\,dT. \tag{10}$$

or

$$\frac{S(T)}{N}\frac{\mathrm{d}Y}{\mathrm{d}T} = Q(T). \qquad (11)$$

We assume here that the product yield from reaction of the recoil atoms or secondary electrons is negligibly small since their kinetic energy is no more sufficient in the majority of the case to initiate further chemical reactions. The cross sections, $Q(T)$, for producing NO_2^- from KNO_3 may be deduced from the slope of the Y-T curves of Fig. 5 and the total stopping-power values presented in Fig. 6 with the aid of Eq. 11. The results are included in Fig. 7; The cross sections for He^+, Ar^+, and Xe^+ ions at 100 keV are $5.7\times10^{-20}\,m^2$, $12.6\times10^{-20}\,m^2$, and $22.0\times10^{-20}\,m^2$, respectively, and they slightly depend on the ion energy T. These values are comparable to the cross sections estimated from the known atomic radius of He, Ar, and Xe, respectively.

Chemical Effectiveness of the Electronic and Nuclear Energy Losses in the Decomposition of Potassium Nitrate. Consider that an ion of the energy T travels a unit distance in the solid (KNO_3). From Eq. 2, the number of the product per unit path length of the ion of the energy at T is $N\,Q(T)$ where N is the number density of the target molecule. The energy expended in this reaction is provided from the energy deposited to this zone (=the unit path length) from the traversing ion, i.e., the total stopping power, $S_t=S_e+S_n$. If we designate the effectiveness of the energy contributed from S_e and S_n for the chemical reaction as f_e and f_n, respectively, the fraction of the deposited energy which is utilized to nitrite production, $N\,Q(T)$, is $f_eS_e+f_nS_n$. Thus, one may expect a linear relationship holds between $Q(T)$ and the value of $(f_eS_e+f_nS_n)/(f_e+f_n)$ or $(S_e+pS_n)/(1+p)$ where p represent f_n/f_t. In Fig. 8 are plotted the value of $Q(T)$ (shown in Fig. 7) as a function of $(S_e+pS_n)N^{-1}(1+p)^{-1}$ with p as a parameter. It is clearly demonstrated that an expected linear relationship holds when p is around 0.2. This suggests that, in the decomposition of KNO_3 due to the transmitted energy from the incident ion, an electronic energy is about five times more effective than a nuclear energy.

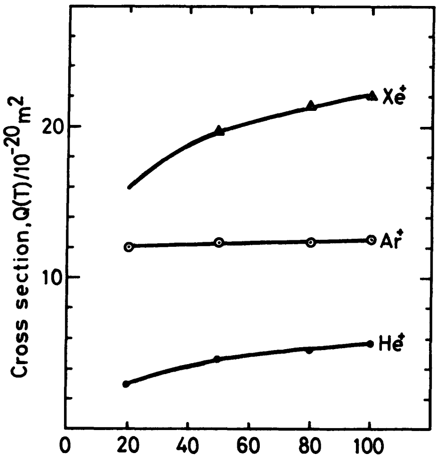

Fig. 7. Cross sections, $Q(T)$, for producing NO_2^- from KNO_3 for He^+, Ar^+, and Xe^+ ions in the energy range from 20 to 100 keV.

Mechanism of the Reaction. Mechanism of decomposition of the radiolyzed nitrates have been studied in many works.[5-11] An important role of atomic oxygen as an intermediate has repeatedly been emphasized (Reaction 1).[7-9]

Elastic "nuclear" collisions may lead to atomic displacements in potassium nitrate. However,the energy transmitted to potassium ions is most probably dissipated as heat; the collision with NO_3^- does not necessarily lead to breaking of the N-O bond. The momentum large enough to break the bond must be effectively trasferred to an O atom (the dissociation energy of the N-O bond is reported to be 3.9 eV[19]). Threshold energies for displacement of O-atoms from the oxide lattices, i.e. ZnO and MgO, are reported to be around 60 to 90 eV.[20] Though, a corresponding energy for KNO_3 has not yet been reported, it is very likely to exceed greatly the dissociation energy of the N-O bond. Thus, it is not surprising to notice that only a small portion of the deposited energy is converted to chemical energy and the remaining energy is degraded to thermal energy.

On the other hand, inelastic collisions may pro-

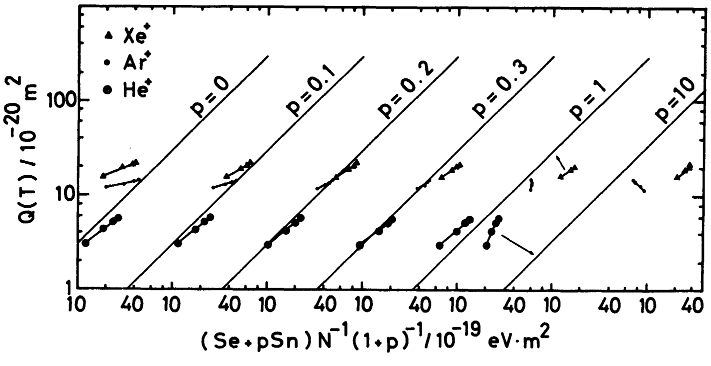

Fig. 8. Test of the linear relationship between $Q(T)$ and $(S_e+pS_n)N^{-1}(1+p)^{-1}$ with p as a parameter; Data taken from Figs. 6 and 7.

duce electronic excited states of the NO_3^- ion. A weak ($\pi^* \leftarrow n$) transition at about 4.1 eV and an allowed ($\pi^* \leftarrow \pi$) transition at about 6.2 eV are well-known.[21,22] These transitions may not lead to the N–O bond breaking, however, since in these transitions an electron is removed from an orbital which is not strongly bonding in nature. An oxygen atom, if it generates without sufficient kinetic energy, will not necessarily escape the parent NO_3^- group owing to some kind of a "cage effect."[10] Excitation of an electron from a bonding (=sp^2 hybrid) orbital is much more likely responsible for the bond dissociation. Excitations of an N- or O-core orbital followed by Auger processes[23] may be even more effective for the bond breaking. A dissociated O-atom may react with other NO_3^- ions,[7]

$$NO_3^- + O \longrightarrow NO_2^- + O_2 \qquad (12)$$

or it may react with the NO_2^- ions produced (see Reaction 3):

$$NO_2^- + O \longrightarrow NO_3^-. \qquad (13)$$

Reactions 12 and 13 have been studied in aqueous solutions and their rate constants relative to that for O_2 were reported to be 5.6 and 37, respectively.[24]

In both cases, i.e. elastic and inelastic collisions, an actual mechanism is probably more complex than above mentionned, possibly involving reactions of several ionic and free radical species. The cross sections which we have derived for the first time in this paper are for an overall reaction to give nitrite ions. Since the occurrence of the many thermal reactions are the same for the both cases, one may possibly state that an inelastic (=electronic) excitation is five times more efficient than an elastic (=atomic displacement) collision for the dissociation of the N–O bond in the solid potassium nitrate.

References

1) Part II: K. Furukawa and S. Ohno, *Bull. Chem. Soc. Jpn.*, **58**, 1831 (1985).

2) J. Kistemaker, F. J. De Heer, J. Sanders, and C. Snoek, "Radiation Research," ed by G. Silini, North-Holland, Amsterdam (1967), p. 68.

3) G. Dearnaley, J. H. Freeman, R. S. Nelson, and J. Stephen, "Ion Implantation," North-Holland, Amsterdam (1973).

4) O. Puglisi, G. Marletta, A. Torrisi, G. Foti, and L. Torrisi, *Radiat. Eff.*, **65**, 11 (1982).

5) J. Cunningham, *J. Phys. Chem.*, **65**, 628 (1961); *ibid.*, **70**, 30 (1966).

6) T. H. Chen and E. R. Johnson, *J. Phys. Chem.*, **66**, 755, 2249 (1962).

7) C. J. Hochanadel, *Radiat. Res.*, **16**, 286 (1962).

8) H. B. Pogge and F. T. Jones, *J. Phys. Chem.*, **74**, 1700 (1970).

9) J. Kalecinski, *Int. J. Radiat. Phys. Chem.*, **4**, 171, 181 (1972).

10) E. Chandunni and S. M. K. Nair, *Radiat. Eff. Lett.*, **58**, 5 (1981).

11) S. R. Logan and W. J. Moore, *J. Phys. Chem.*, **67**, 1042 (1963).

12) T. Sasaki, R. S. Williams, J. S. Wong, and D. A. Shirley, *J. Chem. Phys.*, **68**, 2718 (1978).

13) J. Lindhard and M. Scharff, *Phys. Rev.*, **124**, 128 (1961).

14) J. Lindhard, M. Scharff, and H, E. Schiφtt, *Mat. Fys. Medd. Dan. Vid. Selsk.*, **33**, No. 14 (1963).

15) J. F. Ziegler, "The Stopping and Ranges of Ions in Matter," Pergamon Press, New York (1980), Vol. 5.

16) K. Furukawa and S. Ohno, "100 kV-Ion Accelerator for Study of Chemical Reactions," JAERI-M 85-110 (1985).

17) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. 2, D. Van Nostrand, New York (1955), p. 802.

18) L. V. Spencer and U. Fano, *Phys. Rev.*, **93**, 1172 (1954).

19) Calculated using the constants of heat of formation: "CRC Handbook of Chemistry and Physics," ed by R. C. Weast, CRC Press, Florida (1985), p. D-50.

20) G. P. Pells, *Radiat. Eff.*, **64**, 71 (1982).

21) a) R. F. Barrow and A. J. Merer, Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, ed by A. A. Eldridge et al., Longsmans (1967), Vol. VIII, Supplement II, p. 479; b) "Kagaku Benran," 3rd ed., ed by Chemical Society of Japan, II-595 (1985).

22) E. V. Sayre, *J. Chem. Phys.*, **31**, 73 (1959).

23) M. L. Knotek and P. J. Feibelman, *Surface Sci.*, **90**, 78 (1979); G. Stöcklin, "Radiation Research," ed by S. Okada et al., Jpn. Assoc. Radiat. Res, Tokyo (1979), p. 382.

24) O. Amichai and O. Tereinin, *Chem. Phys, Lett,*, **3**, 611 (1969).