dimensions: $a = 9.649$ Å and $c = 7.181$ Å. The indexing gives a unit-cell volume of 579 Å^3 and with the number of molecules per unit cell $z = 2$, a calculated density value of 5.68 g cm^{-3} was obtained which is in good agreement with the experimental density value of 5.61 g cm^{-3}.

The cell parameters proposed for the compound $Ce_{10}Si_6O_{24}N_2$ are found to be close to the values for the analogous silicon lanthanide oxynitride [1] and silicon yttrium oxynitride [4]. As can be expected, the lattice parameter values show an increasing trend with increasing "ionic" radii of the rare-earth cation Ln^{3+} and Y^{3+}. It is noteworthy that a cerium oxysilico–apatite having a formula of $Ce_{4.67}(SiO_4)_3O$ which occurs in the pseudobinary join SiO_2–Ce_2O_3 has a fluorapatite structure [6] similar to that of the nitrogen-containing apatite phase $Ce_5(SiO_4)_3N$ reported here and thus the X-ray diffraction pattern for one could be easily mistaken for the other. The nature and characteristics of various apatite-type phases in the system Ce–Si–O–N and compatibility relations between them will be described in detail in a separate publication.

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On the adsorption processes in the selective etching of MgO and CaF_2 crystals

In a detailed study of the etching of LiF, Gilman *et al.* [1] found trivalent cations in water to be effective agents in the formation of etch pits at dislocation sites. It was suggested that these cations chemisorb at kink sites in a ledge and thus inhibit its motion. Since their work, many observations [2–4] of the etching phenomenon have been reported on alkali halides, which indicate that the inhibition process is not simple chemisorption. Etchants of semiconductors and metals are still more complicated and, consequently, are less suited for the study of the mechanism of adsorption and etch-pit formation. Etchants of periclase, fluorites and barytes are aqueous acidic solutions and hence etching studies on these crystals may be hoped to provide considerably fruitful information on the dissolution process.

In the present communication the adsorption process taking place on MgO and CaF_2 crystals is analysed from a study of the dependence of selective etch rates on the concentration and temperature of HCl. Etching was conducted on {1 0 0} faces of MgO and {1 1 1} faces of CaF_2 crystals in the temperature range 20 to 80° C. The rate of lateral etching, v_t, at dislocations in MgO was determined using the procedure employed earlier [5]. In the case of CaF_2, the rate was computed from the distance between a side and the opposite corner of a triangular etch pit, and from the distance between the opposite sides of a hexagonal pit.

The dependence of v_t on concentration, c, at different etchant temperature is shown in Figs. 1 and 2 for MgO and CaF_2 crystals, respectively. It may be noted from these figures that v_t attains a maximum value, v_{max}, and then decreases with a further increase in c. The values of v_{max} and c_{max} depend on the nature of the acid (Fig. 2), the crystal, and on the etching temperature. The value of c_{max} decreases with an increase in etching temperature.

It was also observed that the etch-pit mor-

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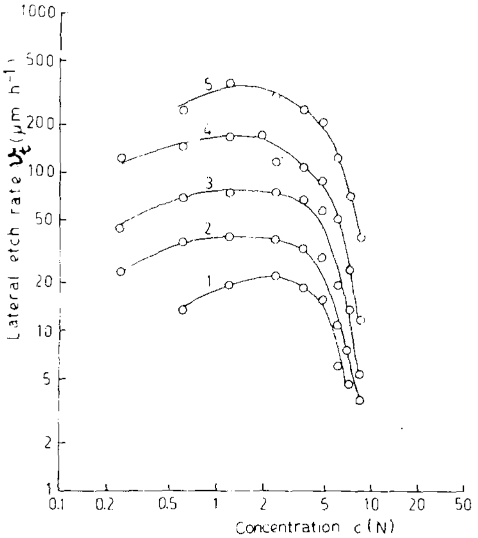

Figure 1 Graph showing the dependence of v_t for MgO on c of HCl at different temperatures: (1) 29° C, (2) 40° C, (3) 50.5° C and (4) 63° C and (5) 79.5° C.

phology varies with increase in acid concentration. In MgO at low concentrations, ⟨1 1 0⟩ pits and, at high concentrations, ⟨1 0 0⟩ pits are formed. In the neighbourhood of c_{max}, pits are circular. In the case of CaF_2, pits are triangular at low concentrations, while they are hexagonal around and beyond c_{max} (Fig. 3).

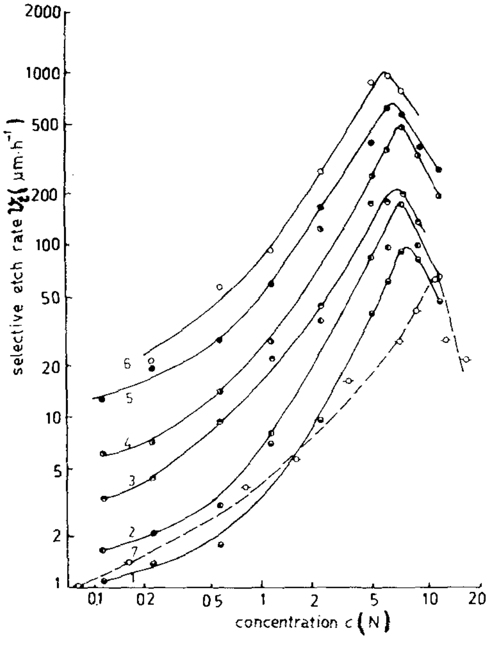

Figure 2 Plots of the dependence of v_t on c of HCl (1–6) and HNO_3 (7) for CaF_2. Temperatures of etching: (1) 29° C, (2) 35° C, (3) 40° C, (4) 50° C, (5) 60° C, (6) 72° C and (7) 29° C.

The appearance of peaks in the curves of etch rate versus $CuCl_2 \cdot 2H_2O$ concentration in alcohols was first observed in CsI crystals [3, 4] and subsequently in the curves of etch rate versus acid concentration in the case of MgO crystals [5]. The maximum corresponds to that concentration of $CuCl_2 \cdot 2H_2O$, and of HNO_3 and HCl at which octagonal or circular pits were observed to form. In CsI [3, 4] the behaviour was explained on the basis of the influence of copper complexes on the nucleation and movement of dissolution steps. The appearance of maxima in MgO was attributed to the adsorption of acid and reaction products [5]. Here we apply an approach [6] which involves the velocity of acid ions, their adsorption on the crystal surface, formation of some complex and its adsorption on the crystal surface, and discuss the nature of adsorption processes.

Assume that the processes of dissolution proceeds as follows [6]:

$$2\mathrm{MgO} + 2\mathrm{H}^+ + 2\mathrm{An}^- \overset{1}{\rightleftharpoons}$$

$$\overset{1}{\rightleftharpoons} \mathrm{MgO}\begin{matrix}\cdot\,\mathrm{H}\cdots\mathrm{An}\,\cdot\\ \cdot\,\mathrm{H}\cdots\mathrm{An}\,\cdot\end{matrix}\mathrm{MgO} \overset{2}{\rightleftharpoons}$$

(unadsorbed)

$$\overset{2}{\rightleftharpoons} \mathrm{MgO}\begin{matrix}\cdot\,\mathrm{H}\cdots\mathrm{An}\,\cdot\\ \cdot\,\mathrm{H}\cdots\mathrm{An}\,\cdot\end{matrix}\mathrm{MgO} \overset{3}{\rightleftharpoons}$$

(adsorbed)

$$\overset{3}{\rightleftharpoons} \text{activated complex} \longrightarrow$$

$$\longrightarrow \text{products} \qquad (1)$$

Here An^- represents an anion. The number n_5 of the complex molecules on the surface is [6]

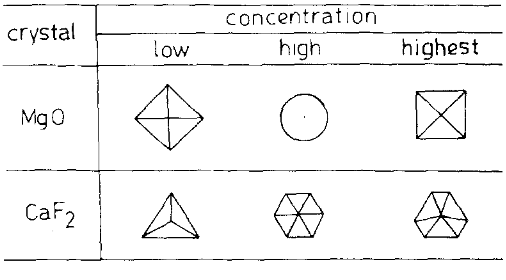

Figure 3 Change in the morphology of etch pits with HCl concentration. High concentration implies the range of maximum etch rates.

$$n_5 = \frac{\phi n_{\mathrm{H}}}{Zr^{1/4}}\left(\frac{3kT}{m_{\mathrm{H}}}\right)^{1/2} \times \exp\left[-\left\{\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3'\right\}/kT\right], \qquad (2)$$

where n_{H} is the concentration of H^+ ions in the etchant, Z the number of free bonds on the surface, m_{H} the mass of an H^+ ion, r the ratio of mass of an anion to that of H^+ ion, E_1' and E_2' the energies required for the capture and migration of a pair of each H^+ and An^- ion respectively, on the surface, E_3' the energy of formation of an unadsorbed complex molecule

$$\mathrm{MgO}\begin{array}{c}\cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\\ \cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\end{array}\mathrm{MgO},$$

and $\phi = \alpha^{-1.9}c^{0.8}$ [6] for HCl. α and c appearing in the equation are degree of dissociation and concentration of the acid, respectively. It can be shown that for various peak values of c of HCl, $\phi \approx 25$, and $r^{1/4} = 2.44$. Hence for $Z = 1$, one obtains

$$\frac{n_5}{n_{\mathrm{H}}} = 10\left(\frac{3kT}{m_{\mathrm{H}}}\right)^{1/2} \times \exp\left[-\left\{\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3'\right\}/kT\right].$$

Replacing the numbers n_5 and n_{H} by the corresponding concentrations of

$$\mathrm{MgO}\begin{array}{c}\cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\\ \cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\end{array}\mathrm{MgO}\ \text{(unadsorbed)}$$

and acid, we have

$$\frac{c_{\mathrm{com}}}{c} = 10\left(\frac{3kT}{m_{\mathrm{H}}}\right)^{1/2} \times \exp\left[-\left\{\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3'\right\}/kT\right]. \qquad (3)$$

The equilibrium constants corresponding to steps 1 and 2 of Equation 1 are

$$K_1 = \frac{\left[\mathrm{MgO}\begin{array}{c}\cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\\ \cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\end{array}\mathrm{MgO}\right]_{\mathrm{unads}}}{[\mathrm{H}]^2[\mathrm{Cl}]^2} = \frac{c_{\mathrm{com}}}{\alpha^4c^4},$$

$$K_2 = \frac{\left[\mathrm{MgO}\begin{array}{c}\cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\\ \cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\end{array}\mathrm{MgO}\right]_{\mathrm{ads}}}{\left[\mathrm{MgO}\begin{array}{c}\cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\\ \cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\end{array}\mathrm{MgO}\right]_{\mathrm{unads}}},$$

whence

$$K_1 = \frac{c_{\mathrm{com}}}{\alpha^4c^4}, \qquad (4)$$

$$K_2 = \frac{1}{K_1\alpha^4c^4}. \qquad (5)$$

Using Equation 4, Equation 3 may be written in the form

$$K_1\alpha^3c^3 = 10\left(\frac{3kT}{m_{\mathrm{H}}}\right)^{1/2} \times \exp\left[-\left\{\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3'\right\}/kT\right]. \qquad (6)$$

If E_4 is the energy of adsorption of

$$\mathrm{MgO}\begin{array}{c}\cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\\ \cdot\cdot\mathrm{H}\cdots\mathrm{An}\cdot\cdot\end{array}\mathrm{MgO},$$

the adsorption equilibrium constant is given by [7]

$$K_2 = \frac{1}{K_1\alpha^4c^4} = \exp\left[\Delta S^0/R\right]\exp\left[-E_4'/kT\right]. \qquad (7)$$

where ΔS^0 is the change in entropy due to adsorption.

From Equation 6, K_1 corresponding to the peak values of the acid concentration at different temperatures, and $\{\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3'\}$* may be estimated. Substituting the values of K_1 and c in Equation 5, K_2 at different temperatures may also be calculated. The calculated values of K_1, K_2 and $\{\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3'\}$ are given in Table I. Then from a plot of $\log K_2$ versus $1/T$ (Fig. 4), E_4' may be determined. The values of $\{\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3'\}$ and E_4' for the selective etching of MgO and CaF_2 in HCl are listed in Table II.

TABLE I Estimated values of K_1, K_2 and $\{\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3'\} = E$ for the etching of MgO and CaF_2 crystals

	T (K)	K_1	K_2
MgO	302.5	1.02	65.5
$E = 0.17$ eV	313.0	1.49	71.8
	323.5	1.53	92.6
	336.0	2.31	102.6
	352.5	2.31	142.2
CaF_2	302	4.60	1.59
$E = 0.23$ eV	308	3.87	2.10
	313	3.24	2.67
	323	1.89	5.00
	333	1.72	6.49
	345	1.01	11.90

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* A higher value of $\{\tfrac{1}{4}(E_1' + E_2') + \tfrac{1}{2}E_3'\}$ gives a higher K_1 and, consequently, a lower K_2. This leads to a higher E_4'. However, this increase in E_4' is not appreciable.

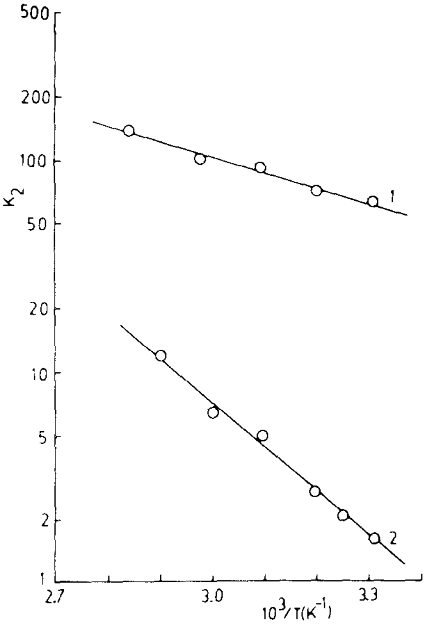

Figure 4 Plots of the dependence of $\log K_2$ on $1/T$ for (1) MgO and (2) CaF_2.

Assuming that the energy of the formation of the complex molecule and the energy of the migration of H^+ and An^- on a surface are negligible, $\frac{1}{2}(E'_1 + E'_2)$ may be taken as the energy of adsorption of a pair of each H^+ and An^- ions on the surface. Now the heat of physical adsorption is usually below 0.4 eV [8]. Therefore, it may be concluded that for MgO and CaF_2 in the region where peaks in the rate versus concentration curves develop, adsorption of an individual H^+ and Cl^- and of the intermediate complex is physical. The process is also associated with an increase in entropy (Table II).

TABLE II Energies of adsorption of a pair of H^+ and Cl^- ions and of the complex, and the entropy change in the etching of MgO and CaF_2 crystals

Crystal	$E'_1 + E'^*_2$ (eV)	E'_4 (eV)	ΔS^0 (kcal mol^{-1} K^{-1})
MgO	0.68	0.15	6.8
CaF_2	0.92	0.42	4.1

* Assuming that $E_3 \approx 0$.

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Electron microscopic examination of splat-cooled foils of Sn–Sb–Ag Alloy

By very rapidly cooling from the melt (so-called liquisol quenching) Klement *et al.* [1] were able to solidify Au–Si alloys near the eutectic composition in an amorphous state. This discovery has since been followed by the production of large number of amorphous phases in a variety of binary and ternary alloy systems using liquid quenching [2–6]. Added to these exciting results, researchers in this field have also observed unusual properties in materials prepared by liquisol quenching, such as striking improvements in the mechanical properties and unexpected semiconducting and superconducting properties. One should note the works

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