

## Surface charges and subsurface space-charge distribution in magnesium oxides containing dissolved traces of water

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MgO crystals which contain dissolved traces of H<sub>2</sub>O eventually acquire an excess oxygen content, MgO<sub>1+δ</sub>, because OH<sup>-</sup> pairs, associated with cation vacancies, convert in part into molecular H<sub>2</sub> and peroxy anions, O<sub>2</sub><sup>2-</sup>. While H<sub>2</sub> molecules are lost from the crystal, the vacancy-bound O<sub>2</sub><sup>2-</sup> remain as spin-paired, self-trapped positive holes. Probably at this stage the MgO surface is negatively charged. Around 800 K the O<sub>2</sub><sup>2-</sup> decay, releasing unbound positive holes, i.e., highly mobile O<sup>-</sup> states. They lead to an oxygen release from the crystal surface and a positive surface charge. With the assumption that the vacancy-bound holes are essentially immobile the space-charge distribution in the subsurface region and the associated electric field and potential were calculated for different temperatures and as a function of charge carrier concentration. The width of the space-charge region is of the order of 10–50 nm, decreasing with increasing concentration, while the field at the surface increases. At a concentration as small as 10–20 ppm the field at the surface is of the order of  $3.8 \times 10^7$  V m<sup>-1</sup>. At higher temperatures when cation vacancies are mobilized, the negatively charged bound holes will diffuse and drift toward the surface modifying the surface charge and subsurface space-charge layer. When all excess oxygen and excess cation vacancies are annealed out the MgO surface will probably again become negatively charged.

### I. INTRODUCTION

Frenkel<sup>1</sup> and Lehovc<sup>2</sup> showed that in thermodynamic equilibrium the surface of an ionic crystal will always, as a rule, carry an electric charge resulting from the presence of excess ions of one sign. The surface charge is then compensated by a space-charge layer of the opposite sign beneath the surface. The surface/subsurface dipole region arises from the fact that, in a crystal where Schottky disorder prevails, the free energies of formation are usually different for the cation and the anion vacancies. If the free energy necessary to form a cation vacancy is less than that required for an anion vacancy, the surface becomes negatively charged and the subsurface space-charge layer will carry a positive sign, so that overall charge neutrality is maintained.

This theory has been applied mainly to alkali halides, the model substances for Schottky disorder. It has been extended to grain boundaries and dislocations.<sup>3–5</sup> Kliewer and Koehler<sup>6</sup> treated the important case of divalent cation impurities in alkali halides. They represent excess positive charges and thus introduce an equimolar concentration of extrinsic cation vacancies. Kingery<sup>7,8</sup> applied the same formalism to alkaline-earth oxides doped with heterovalent cation impurities. The question of whether the surface of alkaline-earth oxide crystals is positively or negatively charged, implying a negatively and positively charged subsurface space-charge layer, respectively, is somewhat ambiguous. Experimental data<sup>9</sup> show that trivalent cations, for instance Sc<sup>3+</sup>, which has the same ionic size as Mg<sup>2+</sup>, becomes enriched in the subsurface region of MgO. The width of the segregated layer, 10–20 nm, agrees with the width of the space-charge layer calculated for Ca-doped NaCl.<sup>6</sup> The sign is positive,

implying a negatively charged surface.

The phenomenon of surface segregation in ionic crystals has also been treated under the aspect of strain relaxation.<sup>10,11</sup> Large homovalent cations, for instance, Ca<sup>2+</sup> in MgO, have been shown to segregate strongly to the surface.<sup>11,12</sup> The absence of a marked subsurface concentration profile which would reach far into the bulk suggests that no long-range interaction exists in this particular case. Long-range interaction may arise, if both driving forces are jointly acting, surface charge and strain relaxation,<sup>10,11</sup> and if in addition the segregating impurities form dipolar defects.<sup>13,14</sup>

On different levels of sophistication the ionic model has proven to be quite successful for the prediction of material properties of oxides, including surface phenomena.<sup>10,11</sup> In all cases discussed in the literature, the assumption was made that oxides are sufficiently well described by an array of fixed-valency O<sup>2-</sup> anions in which cations of different valencies are embedded. No consideration was given to the possibility that electronic defects may exist in the O<sup>2-</sup> sublattice which would render the assumption of fixed-valency O<sup>2-</sup> anions invalid.

The O<sup>-</sup> state represents a defect electron or positive hole, sometimes called an oxygen-associated hole center (OHC).<sup>15,16</sup> It is important because of its paramagnetism.<sup>17</sup> The O<sup>-</sup> state is usually introduced into solids by ionizing radiation and is often considered to be rather unstable thermally. In this paper we shall focus our attention on various aspects of the O<sup>-</sup> state, and on its occurrence in an ionic oxide such as MgO, without calling for the effect of ionizing radiation.

Throughout this paper we shall use a slightly modified defect notation due to Kröger.<sup>18</sup> It designates excess positive and excess negative charges by dot (·) and prime (').

Double overdot (") and double prime (") represent two positive and two negative excess charges, respectively. Any lattice site which possesses the correct charge with respect to the ideal structure is called "neutral" and designated by a cross (x).  $V$  stands for vacancy and index  $i$  for interstitial. This nomenclature has the advantage of being unambiguous for simple structures.  $V''_{\text{Mg}}$ , for instance, designates an  $\text{Mg}^{2+}$  vacancy, while  $\text{Fe}^x_{\text{Mg}}$  is an  $\text{Fe}^{2+}$  ion on an  $\text{Mg}^{2+}$  lattice site. If we want to describe an  $\text{Fe}^{3+}$  ion on an  $\text{Mg}^{2+}$  lattice site, the symbol is  $\text{Fe}^+_{\text{Mg}}$ .  $\text{O}^{2-}$  ions on their usual lattice sites are designated by  $\text{O}^x$ , but an  $\text{O}^-$  on an  $\text{O}^{2-}$  lattice site is written as  $\text{O}^-$ . The Kröger symbols can be combined to reflect certain specific defect configurations. For instance, a peroxy anion,  $\text{O}_2^{2-}$ , substituting for two  $\text{O}^{2-}$  ions, may be written as  $(\text{O}^-)_2$ . If the peroxy anion is associated with a divalent cation vacancy, the defect becomes neutral with respect to the perfect lattice,  $(\text{O}^-)_2 V''_{\text{Mg}}$  which—in physical terminology—

represents a self-trapped positive hole pair, spin-paired and hence diamagnetic.

Figures 1(a)–1(c) depict the three  $\text{O}^-$ -type defects for the (100) plane of  $\text{MgO}$ .

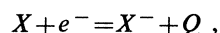
(a) The unbound paramagnetic  $\text{O}^-$  state, viz., a single positive hole or defect electron on an  $\text{O}^{2-}$  anion,  $\text{O}^-$  [later called an "unbound" hole in contrast to the "bound" hole which is associated with an  $\text{Mg}^{2+}$  vacancy,  $(\text{O}^- V''_{\text{Mg}})^x$ ].

(b) The  $\text{O}_2^{2-}$  anion, viz., the self-trapped, diamagnetic positive hole pair which is *not* associated with an  $\text{Mg}^{2+}$  vacancy  $(\text{O}^-)_2$ .

(c) The same  $\text{O}_2^{2-}$  anion associated with, and therefore charge-wise compensated by, an  $\text{Mg}^{2+}$  vacancy,  $(\text{O}^-)_2 V''_{\text{Mg}}$ .

## II. THE $\text{O}^-$ STATE

For an insulator the electron affinity is defined as that energy which must be supplied to take an electron from the top of the valence band out of the crystal to a state of rest at an infinite distance. The electron affinity is positive for all halides  $X$ :



where  $Q$  is a quantity of heat. In the case of oxygen the situation is different. In the first stage,  $\text{O} + e^- = \text{O}^- + Q'$ , and the reaction is exothermal with  $Q' = 1.4$  eV. In the second stage, however, the reaction is strongly endothermal:  $\text{O}^- + e^- = \text{O}^{2-} - Q''$ , with  $Q'' = 8.9$  eV.<sup>19</sup> In other words, a free  $\text{O}^{2-}$  ion would spontaneously emit an electron and convert into the more stable  $\text{O}^-$  state.

This leads to an interesting situation which seems not to have been given much attention so far in solid-state physics: In any predominantly ionic oxide, such as  $\text{MgO}$ , the  $\text{O}^{2-}$  ions are uniquely stabilized by the Coulomb interaction with the positively charged cations, for instance,  $\text{O}^{2-} \cdots \text{Mg}^{2+}$ . If it were not for the Coulomb interaction, we would rather have  $\text{Mg}^{2+}$  combined with two  $\text{O}^-$ , which would give the stoichiometry of a peroxide,  $\text{MgO}_2$ . Alternatively, we can say that the  $\text{O}^{2-}$  state may become unstable in any given ionic oxide structure, if the Coulomb potential is locally perturbed.  $\text{O}^{2-}$  anions may then convert into  $\text{O}^-$ . Candidates for such events are any major defects, such as surfaces, grain boundaries or dislocations, and also point defects such as cation vacancies.

In alkali halides it was the difference between the free energies of formation of cation and anion vacancies which allowed for the calculation of the surface charge: Because, as a rule in alkali halides, cation vacancies have the lower free energy of formation, their surface will carry a negative charge and a compensating positive space-charge layer beneath. This holds for low to intermediate temperatures. At high temperatures, due to entropy effects, a sign reversal is anticipated.<sup>6</sup>

In the alkaline-earth oxides the situation might be very different, at least at low to moderate temperatures when Schottky disorder is not the prevailing mechanism. One has to balance the free energy of formation of the cation vacancies against any energy term which describes the conversion of  $\text{O}^{2-}$  into  $\text{O}^-$ , i.e., the formation of an electronic defect. The difficulty arises from the fact that, while the  $\text{O}^{2-}$ - $\text{O}^-$  conversion will probably not occur in

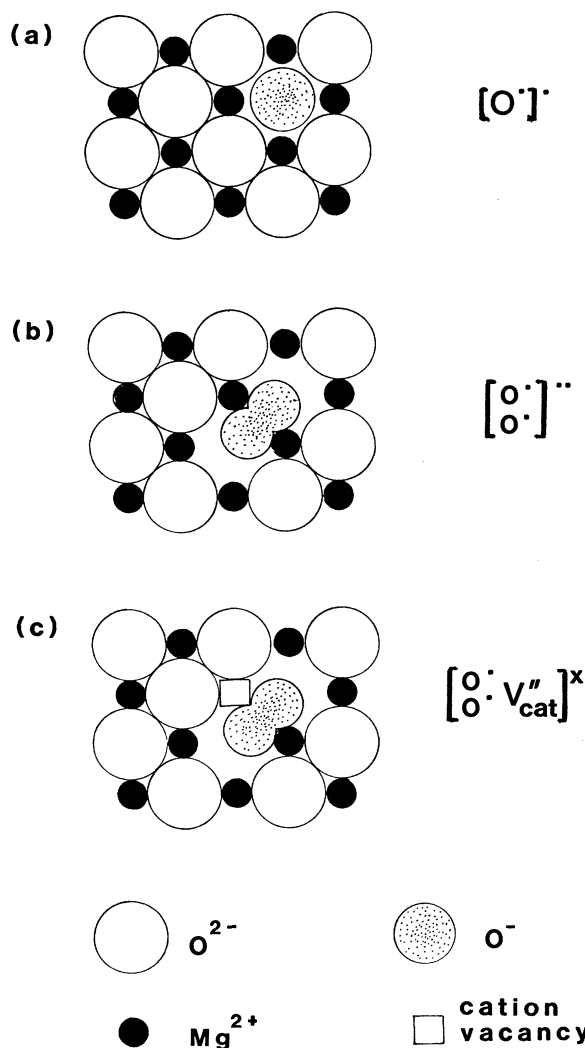


FIG. 1. Positive hole centers depicted for the (100) plane of  $\text{MgO}$ . (a) single positive hole (paramagnetic) corresponding to an  $\text{O}^-$  state; (b) positive hole pair (diamagnetic) without adjacent cation vacancy, corresponding to a peroxy anion  $\text{O}_2^{2-}$ ; (c) same as (b) adjacent to a cation vacancy.

the perfect lattice, it may take place to various degrees wherever the structure is defective. Then, instead of having a well-defined value for the energy of formation of a positive hole, different energy terms will have to be considered for different defect situations. Some of these terms may be considerably smaller, especially near the surface, than the free energy of formation of a cation vacancy. Hence, it is conceptually possible that the surfaces of alkaline-earth oxide crystals are negatively charged with a positive subsurface space-charge layer. At the same time the surface polarity may also change as a function of temperature.

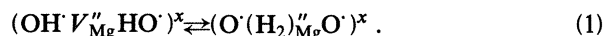
### III. "WATER" AS AN IMPURITY

One impurity in MgO which has been strangely neglected is hydrogen. It derives from dissolved traces of water. The presence of  $\text{OH}^-$  ions in synthetic MgO single crystals has been noted early, as has the presence of molecular  $\text{H}_2$ ,<sup>20-22</sup> but the genetic connection between the two forms of "hydrogen" was unclear. It has been demonstrated experimentally<sup>23-25</sup> that molecular  $\text{H}_2$  can form in MgO and from MgO, doped with  $\text{OH}^-$  ions, without having recourse to transition-metal cation impurities acting as a reducing agent.

For any one  $\text{H}_2\text{O}$  molecule introduced into an MgO crystal one oxygen is added. This necessarily creates an extrinsic cation vacancy  $V_{\text{Mg}}''$ , the charge of which will be preferentially compensated for by the two protons forming  $\text{OH}^-$  anions. This results in the linear neutral defect  $(\text{OH}^- V_{\text{Mg}}'' \text{HO}^-)^x$  shown in Fig. 2 (bottom left).

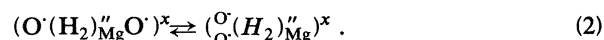
Pope *et al.*<sup>26</sup> have recently carried out extensive calculations for the dissociative chemisorption of molecular  $\text{H}_2$

at the  $V$  center on the (100) surface of MgO. The  $V$  center consists of two separate  $\text{O}^-$  states associated with the  $\text{Mg}^{2+}$  vacancy, and the chemisorption of  $\text{H}_2$  thereon leads to two  $\text{OH}^-$  anions. The activation energy for the  $\text{H}_2$  dissociation was found significantly depressed, hence the potential catalytic importance of this reaction.<sup>26</sup> The surface reaction treated by Pope *et al.*<sup>26</sup> resembles the situation depicted in Fig. 1 (center) for the bulk defect,



It is probably justified to assume that, in the bulk, the reaction according to Eq. (1) will follow a pathway characterized by two potential minima with a finite energy barrier in between, as in the case of the surface reaction.<sup>26</sup> One minimum would correspond to the  $\text{H}_2$  molecule held between two spatially separated  $\text{O}^-$  states, the other to the two  $\text{OH}^-$  anions. The energies of these two configurations in the bulk and the height of the barrier are yet unknown. In order to obtain a crude estimate we may argue as follows.

In order to dissociate two  $\text{OH}^-$  ions into an  $\text{O}^-$  ion plus  $\text{H}$ , approximately  $860 \text{ kJ mole}^{-1}$  must be supplied.<sup>27</sup> About  $460 \text{ kJ mole}^{-1}$  are regained by the recombination of two  $\text{H}$  to  $\text{H}_2$ . The  $V$  center, featuring two separated paramagnetic  $\text{O}^-$  states, may convert into the diamagnetic peroxy anion  $\text{O}_2^{2-}$ , as depicted in Fig. 2 (upper right). Presumably, by spin pairing, the system gains another  $200 \text{ kJ mole}^{-1}$ ,<sup>27</sup>



If the axis of the  $\text{H}_2$  molecule stands perpendicular to the axis of the  $\text{O}_2^{2-}$  anion, the  $\text{H}-\text{H}$  bond becomes polar-

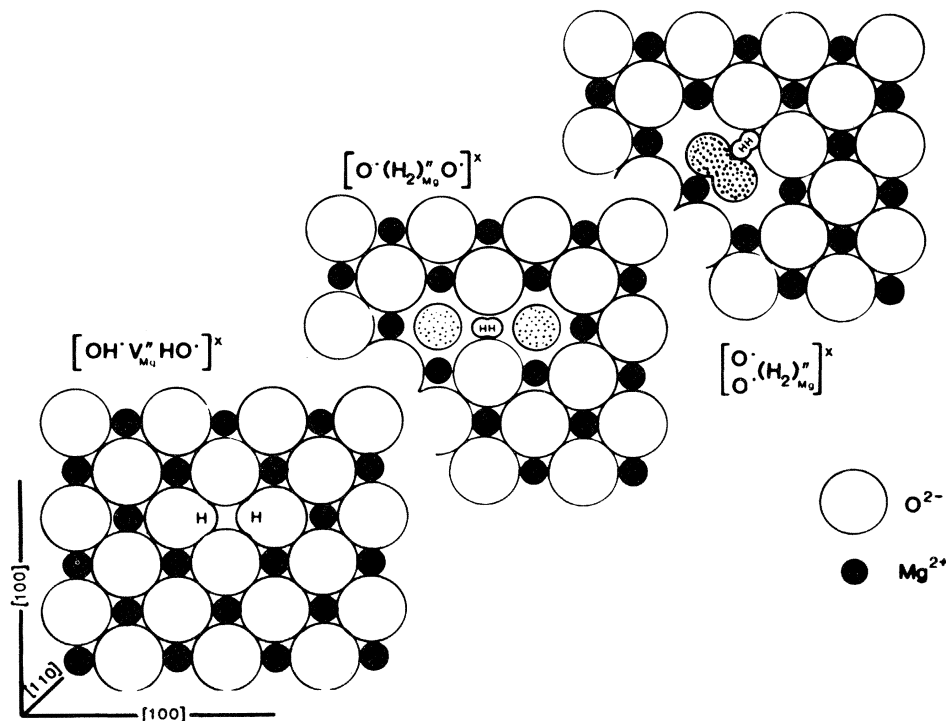


FIG. 2.  $\text{OH}^-$  pair associated with a cation vacancy in the (100) plane of MgO, the predominant defect configuration for the dissolution of  $\text{H}_2\text{O}$ , and its charge-transfer conversion into an  $\text{H}_2$  molecule and an  $\text{O}_2^{2-}$  anion (shown without lattice relaxation).

ized and thus infrared active.<sup>24</sup> Figure 3 shows the weak but conspicuous IR absorption signal around  $4150\text{ cm}^{-1}$  which is due to molecular  $\text{H}_2$  in MgO and the natural mineral olivine,  $(\text{Mg,Fe})_2\text{SiO}_4$ , in which the same type of reaction seems to occur.

The important point to note is that the O-O distance in the peroxy anion is barely  $0.15\text{ nm}$ , as compared to the normal O-O distance between  $\text{O}^{2-}$  in MgO which is close to  $0.3\text{ nm}$ . By volume, the peroxy anion is much smaller, maybe as much as 50%, than the two  $\text{O}^{2-}$  for which it substitutes. Therefore, the surrounding lattice will contract—a process by which the system gains energy. The volume contraction can be expressed in work  $p\,dV$  exerted on the lattice by the local pressure forces  $p = dU/dV$ , where  $dU$  is the elastic strain energy. With the bulk modulus  $\kappa$  being defined as  $\kappa = V\,dp/dV$ , we have  $\kappa = V\,d^2U/dV^2$ . Taking the molar volume as  $2r^3$ , where  $r$  is the radius of  $\text{O}^{2-}$ , we obtain  $\kappa = (1/18r)\,d^2U/dr^2$ . With the bulk modulus of MgO,  $0.16 \times 10^{12}\text{ Pa}$ , and its lattice energy of about  $4000\text{ kJ mole}^{-1}$ , the volume work at 50% local lattice contraction (which is an upper-limit value) amounts to  $180\text{ kJ mole}^{-1}$ . Thus, in terms of energy, the reaction according to Eqs. (1) and (2) is approximately balanced.

An IR study of MgO and CaO single crystals<sup>24,25</sup> indeed led to the conclusion that, in MgO the major fraction of vacancy-associated  $\text{OH}^-$  pairs, maybe as much as 90%, convert into  $\text{H}_2 + \text{O}_2^{2-}$ , even at ambient temperature. In the case of CaO, which has a larger lattice constant, the equilibrium is more on the side of the  $\text{OH}^-$  pair configuration. This is in agreement with the theoretical prediction and with the crude estimate of the energy balance given above.

There is a practical consequence to this internal  $\text{OH}^-$  conversion: If infrared spectroscopy is used to evaluate the “water” content of a given crystal, based on the intensity of the O—H stretching band of  $\text{OH}^-$  anions, the re-

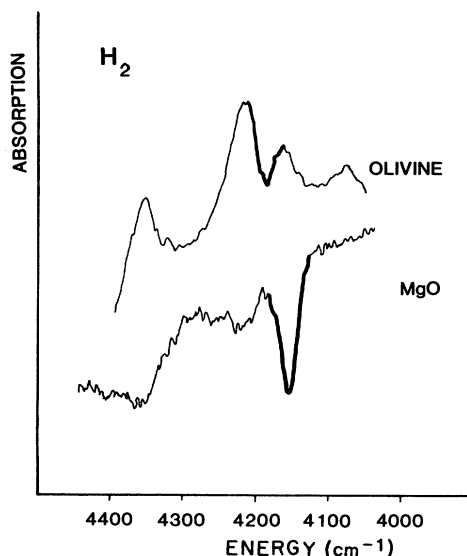


FIG. 3. Infrared absorption signal due to the H—H stretching mode of molecular  $\text{H}_2$  in single crystals of synthetic MgO and (99.99%-purity grade) and natural olivine,  $(\text{Mg,Fe})_2\text{SiO}_4$ .

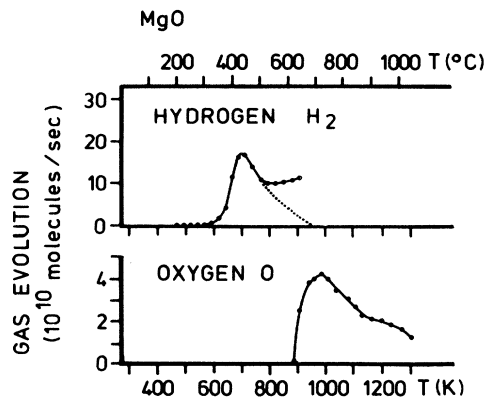
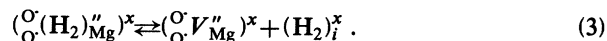


FIG. 4. Sequential release of molecular  $\text{H}_2$  (top) and atomic oxygen (bottom) from finely divided, heavily  $\text{OH}^-$ -doped MgO produced by decomposing  $\text{Mg}(\text{OH})_2$  (after Ref. 23).

sult may be grossly off depending of how many  $\text{OH}^-$  pairs have converted into  $\text{H}_2$  molecules and peroxy-type configurations.

On the other hand,  $\text{H}_2$  is a neutral molecular species which may leave the cation vacancy site where it has formed according to Eqs. (1) and (2), without upsetting the local charge balance. By entering the interstitial sites the  $\text{H}_2$  molecules are mobilized:



At the same time, the  $\text{H}_2$  molecules induce lattice strains which provide a driving force for surface segregation. We therefore anticipate that molecular  $\text{H}_2$  in the MgO diffuses towards the surface. Eventually, it can leave the surface and escape into the gas phase as demonstrated by Fig. 4 (top), which shows the  $\text{H}_2$  evolution from ultrahigh-purity MgO, finely divided and heavily doped with “water” by decomposing  $\text{Mg}(\text{OH})_2$ .<sup>23</sup> The quantity of  $\text{H}_2$  which evolves corresponds to approximately 500 H per  $10^6$  oxygen. The analysis was carried out in a specially designed all-glass ultrahigh-vacuum system with an all-platinum Omegatron mass filter to minimize side reactions which might produce  $\text{H}_2$  from  $\text{H}_2\text{O}$  decomposition.

Formally, we can treat this case as MgO having dissolved a trace  $\delta$  of  $\text{H}_2\text{O}$  to give a solid solution  $\text{MgO}_{1-\delta}(\text{OH})_{2\delta}$ . If all of the  $\text{OH}^-$  were to convert into  $\text{H}_2 + \text{O}_2^{2-}$ , we can rewrite the formula to  $\text{MgO}_{1-\delta}\text{O}_{2\delta}/(\text{H}_2)_\delta$  where  $\text{O}^\bullet$  symbolizes the  $\text{O}^-$  state. After having lost all the  $\text{H}_2$ , the remaining solid has the composition  $\text{MgO}_{1-\delta}\text{O}_{2\delta}$ . This is simply the formula of an MgO which contains an excess  $\delta$  of oxygen,  $\text{MgO}_{1+\delta}$ . According to Eqs. (1) and (2) this excess oxygen is stored in the structure as peroxy anions associated with extrinsic cation vacancies introduced by the dissolution mechanism of  $\text{H}_2\text{O}$ . The remaining part of this paper will be devoted to role of these peroxy anions, their thermal stability, and their effect upon surface charges.

#### IV. PEROXY DECAY

The peroxy anion in MgO may be viewed in different ways. Chemically, it is a dissolved oxygen atom:

$O^{2-} + O = O_2^{2-}$ . Physically, it is a self-trapped positive hole center formed by two  $O^-$  states which underwent spin-pairing. The trapping site is the cation vacancy, which is chargewise compensated by the presence of the  $O_2^{2-}$  as shown in Eq. (3). It is to be expected that the lattice-bound peroxy anions are not indefinitely stable. Upon heating they will decay.

Two cases can be distinguished: (i) The  $O_2^{2-}$  are at the crystal surface (index  $s$ ) together with their balancing cation vacancy, and (ii) the  $O_2^{2-}$  are in the bulk (index  $b$ ). In the first case, the peroxy anion simply disproportionates into an  $O^{2-}$  anion and an oxygen atom which enters the gas phase. This is what happens when well-known peroxides, for instance,  $BaO_2$ , decompose into  $BaO + \frac{1}{2}O_2$ .<sup>28</sup> In our defect notation the reaction becomes

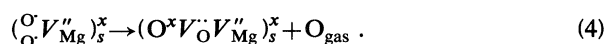


Figure 5(a) depicts Eq. (4) for an unrelaxed (100) surface of MgO. The defect is a Schottky vacancy pair which carries no effective charge. Hence, if this reaction occurs at the surface of the crystal, no surface charge is produced. The oxygen is released at atomic oxygen. Figure 4 (bottom) shows that, indeed, from the finely divided  $MgO_{1+\delta}$ , atomic oxygen evolves at a temperature which is higher than the temperature at which the  $H_2$  evolution occurred. The onset of this O evolution agrees with the known decomposition temperatures of  $BaO_2$  and other peroxides.

In the second case, the peroxy anion decays by releasing an unbound positive hole, an  $O^-$  state which is no longer bound to the cation vacancy,

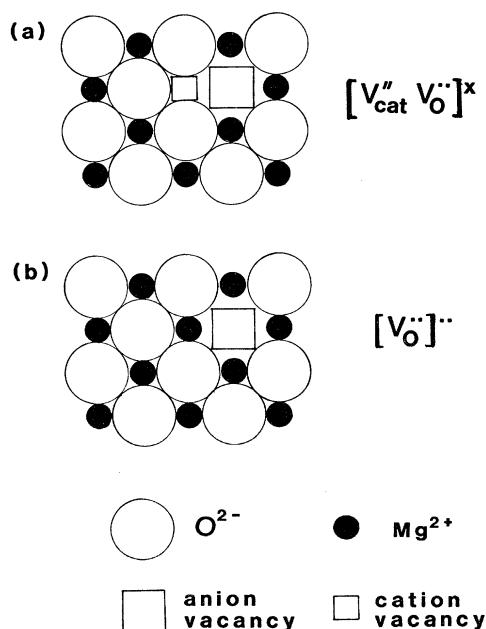
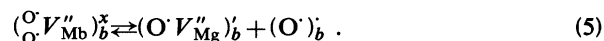


FIG. 5. (a) Formation of a neutral Schottky vacancy pair by the oxygen release from a surface  $O_2^{2-}$  anion associated with a cation vacancy. (b) Formation of an anion vacancy, carrying a double positive charge, by the oxygen release from a surface  $O_2^{2-}$  anion formed from two unbound  $O^-$  states.



The process described by Eq. (5) involves the breaking down of the spin pairing and the formation of two charged defect species. The bound positive hole, i.e., the  $O^-$  state which remains with the cation vacancy, is the well-known  $V^-$  center in the terminology of Sonder and Sibley.<sup>29</sup> It has been extensively studied by electron paramagnetic resonance (EPR) spectroscopy after low temperature exposure to ionizing radiation.<sup>30,31</sup> However, the  $V^-$  center has also been observed in MgO and CaO after a thermal treatment at 1000 K followed by rapid quenching.<sup>22,32</sup> On the other hand, the unbound positive hole is very difficult to detect by EPR on account of its very short relaxation time, which leads to lifetime broadening of the EPR signal.<sup>17</sup> This indicates that the unbound  $O^-$  state is extremely mobile as an electronic defect migrating via the  $O^{2-}$  sublattice. If it reaches the surface, it will become trapped and may recombine with another positive hole forming transient surface peroxy anion,

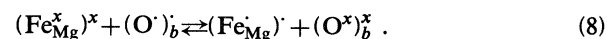


In contrast to Eq. (4), this surface peroxy anion is not chargewise compensated by a cation vacancy, but carries two positive excess charges. If this surface peroxy anion now disproportionates by releasing an oxygen atom, as is depicted by Fig. 5(b), the two positive charges become permanently fixed at the surface,



This charges the surface positively and produces a drift current for all remaining unbound holes away from the surface. The surface charge thus acts as an electrostatic mirror and depletes the unbound holes from the subsurface layer.

Confinement to the bulk may cause the unbound holes to interact with transition-metal impurities, causing their oxidation. If, for instance, an  $Fe^{2+}$  cation traps a hole, it converts into  $Fe^{3+}$ :



Such internal redox reactions can be studied by EPR. Figure 6 shows how the relative concentrations of  $Cr^{3+}$ ,  $Mn^{2+}$ , and  $Fe^{3+}$  change as a function of temperature in MgO.<sup>33</sup> Initially, the three transition-metal impurities are in the oxidation states  $Cr^{3+}$ ,  $Mn^{2+}$ , and  $Fe^{2+}$ . At about 800–900 K, at the same temperature at which the peroxy decay starts as evidenced by Fig. 5 (bottom), oxidation sets in in the bulk to give  $Cr^{4+}$ ,  $Mn^{3+}$  and  $Fe^{3+}$ . Upon cooling, self-reduction occurs, at least in part, as indicated in Fig. 6 (left). This means that the oxidized transition-metal cations release again their trapped positive holes, which, in turn, recombine with the  $V^-$  centers according to Eq. (5) to again form vacancy-bound peroxy anions. Using single crystals or coarse powders (to minimize the oxygen loss from the crystal surfaces), these internal redox reactions can be cycled many times. This suggests that the surface charges generated by a few surface peroxy anions according to Eq. (7) are very effective in keeping

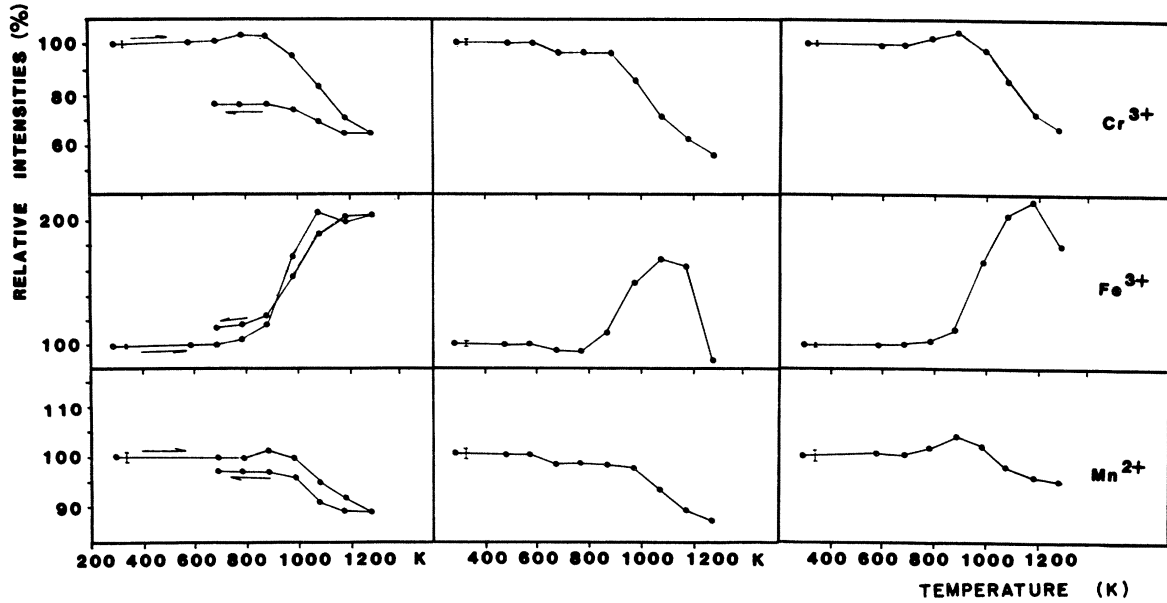


FIG. 6. Internal and, in part, reversible redox reactions involving the transition-metal impurities in  $\text{MgO}$  due to unbound holes, i.e.,  $\text{O}^-$  states, generated by the peroxy decay above 800 K (after Ref. 33).

the unbound holes in the bulk. Only at much higher temperatures, when the cation vacancies start to become mobile and to anneal out by diffusing towards the surface, will the  $\text{MgO}_{1+\delta}$  eventually lose its excess oxygen and become more stoichiometric again.

## V. SURFACE CHARGES AND SUBSURFACE SPACE-CHARGE LAYERS

In order to calculate the space-charge layers we consider the two charged species generated thermally according to Eq. (5): the unbound holes ( $\text{O}^\cdot$ ) and the bound holes ( $\text{O}^\cdot V_{\text{Mg}}''$ ). They carry one positive and one negative charge, respectively. We shall assume that they have widely different mobilities. We designate their concentrations as  $p$  and  $n$ .

The change in concentration  $c(x, t)$  of a diffusing species is related to the difference in the flux of that species arriving at a given point and the flux leaving. Then we have

$$\frac{dc}{dt} = \lim_{dx \rightarrow 0} [I(x-dx) - I(x+dx)],$$

where  $I(x)$  is the flux of the species traveling in the positive- $x$  direction. For random-walk diffusion, Fick's law is obeyed:

$$I(x) = -D \frac{dc}{dx}. \quad (9)$$

If the species drifts under the influence of an electric field  $E$ , then

$$I(x) = \pm \mu c E, \quad (10)$$

where  $\mu$  is the mobility and the sign depends on the carrier charge. The total flux is the sum of the drift and diffusion components. For two oppositely charged carrier concentrations,  $p$  and  $n$ , we have two differential equations which are linked by the drift component,

tions which are linked by the drift component,

$$\frac{\partial p(x, t)}{\partial t} = \mu_p \frac{\partial}{\partial x} (pE) - D_p \frac{\partial^2 p}{\partial x^2}, \quad (11)$$

$$\frac{\partial n(x, t)}{\partial t} = -\mu_n \frac{\partial}{\partial x} (nE) - D_n \frac{\partial^2 n}{\partial x^2}, \quad (12)$$

where

$$\frac{\partial E}{\partial x} = \frac{q}{\epsilon_0 \epsilon} (p - n),$$

with  $q$  being the elementary charge,  $\epsilon_0$  the permittivity of free space ( $8.85 \times 10^{-12} \text{ F m}^{-1}$ ), and  $\epsilon$  the static dielectric constant.

In general, an analytical solution of Eqs. (11) and (12) is not possible. However, if the species  $p$  is much more mobile than the species  $n$ , we have  $D_p \gg D_n$ , and the equations may be decoupled since  $n(x, t_0)$  will not change over the time period required for  $p(x, t_0)$  to reach an equilibrium given by  $\partial p / \partial t = 0$  in Eq. (11). The equilibrium value of  $p(x, t_0)$  may then be inserted and Eq. (12) solved for  $n(x, t_0 + dt)$ . This value, in turn, is set into Eq. (11) to generate a new equilibrium value of  $p(x, t_0 + dt)$ , and the process repeated to calculate  $n(x, t)$ . In practice, Eq. (11) does not need to be solved for every iteration since we shall show that  $p(x, t_0)$  can be approximated by a simple function of  $n(x, t_0)$ . At equilibrium, Eq. (11) is

$$0 = \mu_p \frac{\partial}{\partial x} (pE) - D_p \frac{\partial^2 p}{\partial x^2}. \quad (13)$$

Equation (13) corresponds to assuming that at this stage of the discussion the bound positive holes, the species  $n$  or ( $\text{O}^\cdot V_{\text{Mg}}''$ )' in Eq. (5), are still immobile. Later, turning to higher temperatures, this restriction will be relaxed so that  $n(x, t_0)$  will vary. As mentioned above, the mobility of the bound holes implies a vacancy hopping mechanism.

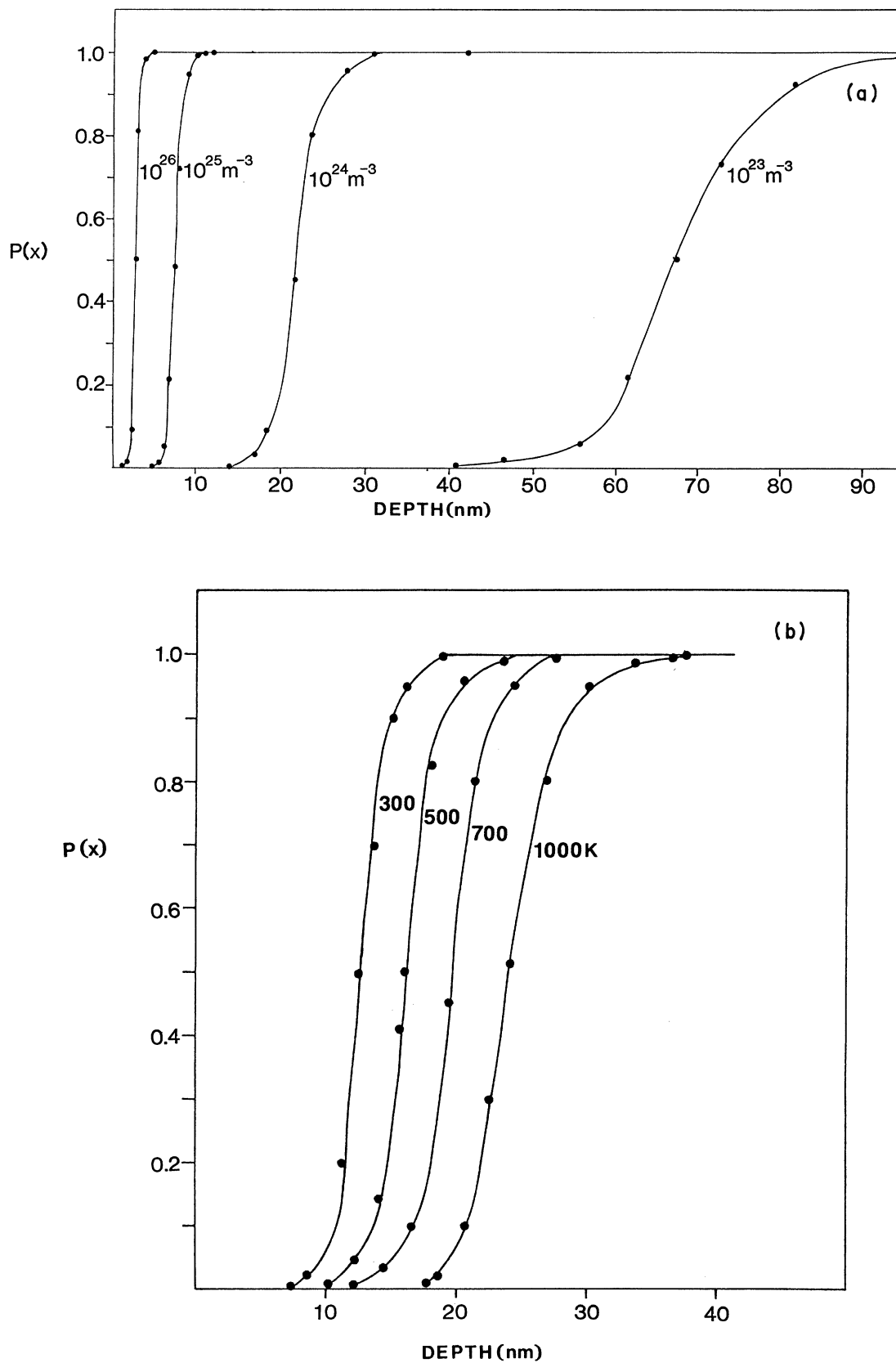


FIG. 7. Equilibrium concentration of unbound holes  $p$  as a function of depth  $x$ : (a) as a function of carrier concentrations at 900 K, and (b) as a function of temperature at a bulk carrier concentration of  $10^{24} \text{ m}^{-3}$ . The near-surface depletion of the unbound holes corresponds to a negative subsurface space-charge region.

The general solution to both cases is found by using a Runge-Kutta numerical algorithm. Equation (13) is transformed into

$$\frac{\partial^2 Y}{\partial x^2} = \frac{q^2}{kT\epsilon_0\epsilon} [\exp(Y) - n(x, t_0)], \quad (14)$$

where  $Y = \ln[p(x, t_0)]$ ,  $E(\infty, t) = 0$ , and  $D_p/\mu_p = kT/q$ . The solution of Eq. (14) is a function of the initial conditions  $Y(x, t_0)$  and  $\dot{Y}(x, t_0)$  which were adjusted so that

$$Y(0, t_0) = 0.$$

Graphical solutions of Eq. (14) are given in Fig. 7(a) for different  $p$ -type charge carrier concentrations at constant temperature, and in Fig. 7(b) for constant concentration but different temperatures. The normalized profiles show that the near-surface region is depleted of  $p$ -type carriers. The width of the depleted region decreases with increasing carrier concentration and increases with increasing temperature.

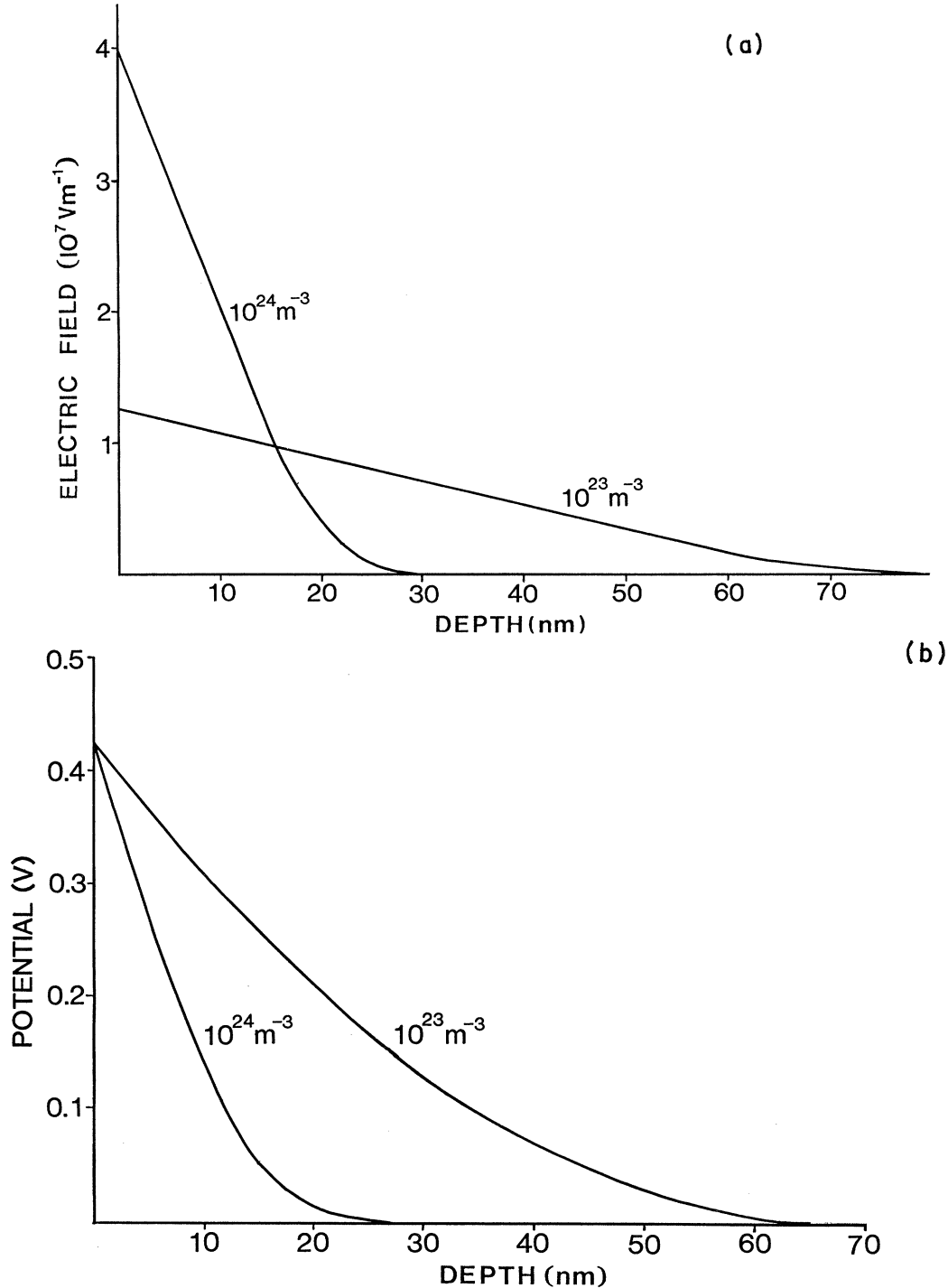


FIG. 8. (a) Subsurface electric field, and (b) subsurface potential for MgO at bulk carrier concentrations of  $10^{23}$  and  $10^{24} \text{ m}^{-3}$ .



The electric field  $E$  generated by the charge unbalance causes the positively charged unbound holes to drift in the positive  $x$  direction in opposition to the diffusion. At equilibrium these two currents will be equal at all points and an equilibrium potential  $-V(x)$  will exist in the solid. This is shown by Figs. 8(a) and 8(b). At the surface the potential amounts to about  $-0.43$  V. The field increases as the root of the carrier concentration. At an unbound hole concentration of  $10^{24} \text{ m}^{-3}$ , corresponding to 100 ppm (which appears to be a very realistic number), the field at the surface reaches  $4 \times 10^7 \text{ V m}^{-1}$ . This value falls within the range of surface potentials calculated for NaCl (Ref. 6) and estimated for MgO (Refs. 7 and 8) from the free energies of formation of cation and anion vacancies. Thus the field reaches values which are at the fringe of the dielectric strength of insulators.

As a result of the high field at the surface the unbound positive holes will be confined to the bulk. A new situation arises if the temperature is raised such that the cation vacancies  $V_{\text{Mg}}''$  start to become mobile. The positive surface field causes them and any other negatively charged, vacancy-bound defects to drift towards the surface, enhancing the flux due to diffusion. Every cation vacancy reaching the surface corresponds to a cation migrating inwards from the surface to fill in the excess cation vacancies in the bulk.

At the same time, every cation vacancy reaching the surface annihilates two positive surface charges. If the bulk still contains sufficient positive holes, i.e., unbound  $\text{O}^-$  states, they can come to the surface, evaporate oxygen according to Eq. (7), and maintain the positive potential.

In order to calculate the subsurface concentration profile of the bound holes, i.e., of the cation vacancies which anneal out at the surface, we have to find an approximate

analytical form for the solution to Eq. (14). As in metal-semiconductor junction theory,<sup>34</sup> a subsurface region of width  $W$  is assumed to be totally depleted of carriers. Therefore

$$p = \begin{cases} n(x, t_0) & \text{for } x > W, \\ 0 & \text{for } x < W, \end{cases} \quad (15)$$

provide the boundary conditions for the desired solution. The width  $W$  of the depleted region with constant doping  $n_0$  is

$$W = \left[ \frac{2\epsilon_0\epsilon}{qn_0} \left[ V_{\text{bi}} - \frac{kT}{q} \right] \right]^{1/2}, \quad (16)$$

where  $V_{\text{bi}}$ , the built-in voltage, is approximately proportional to  $kT/q$ . This yields

$$W \propto (\epsilon T / n_0)^{1/2}. \quad (17)$$

We have fitted our solutions to a relationship of the same form:

$$W_{(p/p_0=0.5)} = 7.12 \times 10^{12} \left[ \frac{\epsilon T}{n(x, t_0)} \right]^{1/2} \quad (18)$$

for  $n(x, t_0) = n_0$ . This formula has also been verified for varying  $n(x, t_0)$ , i.e., if the bound holes are allowed to become mobile. However, the appropriate value of  $n(x, t_0)$  to be inserted in Eq. (18) is not clear. From Fig. 7(a),  $p(x, t)$  is approximately equal to  $n_0$  at  $x = 2W$ , so that the value  $n_0$  in Eq. (18) can be given as  $n(2W, t_0)$ . This results in

$$W = 7.12 \times 10^{12} \left[ \frac{\epsilon T}{n(2W, t_0)} \right]^{1/2}, \quad (19)$$

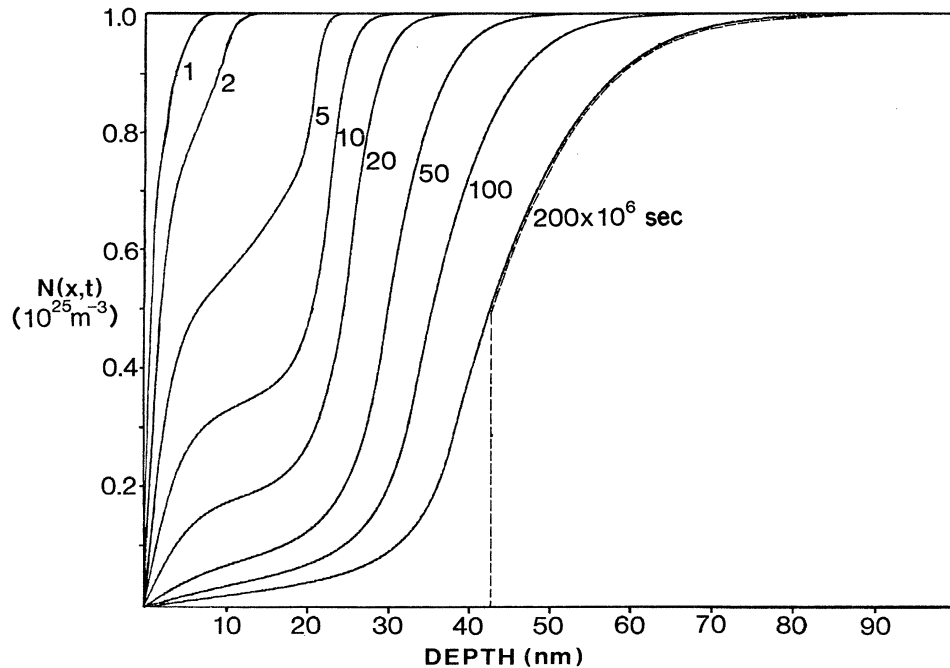


FIG. 9. Subsurface concentration profile of the  $n$ -type carriers (vacancy-bound holes) as a function of time after allowing the cation vacancies to become mobile. The dashed line represents the calculated  $p$ -type carrier concentration after  $2 \times 10^8$  sec.

which can be solved by iteration. Figure 9 shows a set of solutions for  $n(x, t_0)$  as a function of time for an assumed bound hole diffusion coefficient (rate-limited by the diffusion of the vacancies) of  $10^{-24} \text{ m}^2 \text{ sec}^{-1}$  and the static dielectric constant of  $\text{MgO}$ ,  $\epsilon = 9.6$ .

The model may be modified to include the case that the  $\text{MgO}$  contains a fairly high concentration of transition-metal impurities which diffuse faster than  $\text{Mg}^{2+}$  via the cation vacancy hopping mechanism. The profiles in Fig. 9 would then represent the compositional zoning which develops as a result of the inward flux of the most mobile cation species in response to the annealing out of excess cation vacancies. In this case, the surface region would become depleted in the transition-metal oxide component and relatively enriched in the more refractory "pure"  $\text{MgO}$ .

## VI. DISCUSSION

In the case of the alkali halides, featuring Schottky disorder, the sign of the surface charge and subsurface space-charge layer seems to be determined unequivocally by the difference between the free energies of formation of bulk cation and anion vacancies: at low to moderate temperatures the surface charge is negative and balanced by a positive subsurface region. At higher temperatures the sign reverses.<sup>6</sup> The situation is less clear for the alkaline-earth oxides. In this case, complications may arise because, even in a very ionic structure such as that of  $\text{MgO}$ , the  $\text{O}^{2-}$  anions are potentially unstable against releasing an electron and converting into the  $\text{O}^-$  state. What is needed is a perturbation of the Coulomb lattice potential such as that offered in the vicinity of cation vacancies or near the surface of the crystal. An  $\text{O}^-$  represents a positive hole or defect electron in the  $\text{O}^{2-}$  sublattice. If the energy to form  $\text{O}^-$  is small, it is quite possible that a negative surface charge, balanced by a positive subsurface region, will be the "normal" state for the  $\text{MgO}$  surface. This is borne out by the surface segregation behavior of heterovalent impurities in  $\text{MgO}$ .<sup>7-9,13,14</sup>

On the other hand, the discussion of the  $\text{H}_2\text{O}$  dissolution mechanism has shown that peroxy anions,  $\text{O}_2^{2-}$ , may be introduced into the  $\text{MgO}$  far in excess of any intrinsic excess oxygen content as one might expect to introduce by heating the  $\text{MgO}$  in an  $\text{O}_2$  atmosphere. The lattice-bound  $\text{O}_2^{2-}$  anions are self-trapped holes, the trapping site being the divalent cation vacancy needed for the local charge compensation. However, the  $\text{O}_2^{2-}$  anions are thermally stable only up to a certain temperature, typically 800–900 K in  $\text{MgO}$ . Other more stable peroxy-type configurations may exist, perhaps trimers.<sup>35</sup> During their thermal decay the  $\text{O}_2^{2-}$  anions generate unbound and bound holes, i.e., highly mobile  $\text{O}^-$  and the essentially immobile, vacancy-bound  $\text{O}^-$  states. When the unbound  $\text{O}^-$  states reach the crystal surface and release oxygen, they at once create a positive surface charge. If the "normal" charge state for the  $\text{MgO}$  surface is negative as argued above, this would represent a sudden change in surface polarity.

The calculated subsurface space-charge layers presented in the preceding section are instructive inasmuch as they seem to confirm the earlier calculations by Kliewer and Koehler<sup>6</sup> for  $\text{NaCl}$ , even though the starting concept and

the mathematical model were quite different. Kliewer and Koehler<sup>6</sup> used thermodynamic data for the free energies of vacancy formation assuming Schottky disorder. We solved the diffusion and drift equations for unbound and bound holes for the two limiting cases given by the relative mobilities of the two charge-carrying species. We found that unbound holes lead to a high electric field at the surface already at relatively low concentrations, but the magnitude of the field is comparable to the value calculated for  $\text{NaCl}$ ,<sup>6</sup> and also to the value estimated for  $\text{MgO}$  on the basis of the same thermodynamic premises.<sup>7</sup> What is new is that, in our calculation, we can show how the subsurface space-charge layers change as a function of both temperature and carrier concentration. When the concentration increases the profile becomes steeper and more confined to the surface. Concomitantly, the electric field increases at the surface, reaching extremely high values. It should, however, be kept in mind that our mathematical model is a continuum model and does not take into account the atomic structure at the scale of the lattice constant.

In an insulator such as  $\text{MgO}$  the positive surface charge, which is created by the mobile unbound holes and their chemical consequence, the oxygen evolution, will act as an electrostatic mirror. It will tend to preserve the reservoir of mobile  $\text{O}^-$  states in the bulk until the vacancies become mobile at higher temperatures and eventually anneal out at the surface. It is not unexpected to find a  $t^{1/2}$  relationship for the progress of the interface which marks the return of the  $\text{MgO}$  bulk to its intrinsic equilibrium with respect to cation vacancy concentration and excess oxygen content.

The final result of this analysis is that the positive surface charge of the  $\text{MgO}$  is a transient phenomenon due to impurities like traces of dissolved "water" which cannot be avoided under any realistic crystal-growth conditions.<sup>21</sup> This transient phenomenon may, however, dominate over a wide range of temperatures and annealing times. At sufficiently high temperatures and after sufficiently long annealing, the  $\text{MgO}$  surface probably returns to its "normal" charge state, a negative surface charge and a positive subsurface region. The chemical expression of the positive subsurface space charge would then be the build up of the segregation profile of trivalent cation impurities as reported in the literature,<sup>7-9</sup> which, of course, can only be observed after long high-temperature annealing.

This is different for the subsurface segregation of carbon in  $\text{MgO}$  which occurs already at low temperatures, due to the very low activation energy of diffusion for the solute carbon species.<sup>13,14</sup> At low temperatures the unbound holes "go to sleep" by being trapped at the cation vacancy sites in the bulk, forming diamagnetic dimers which we have designated in this paper by their chemical name as peroxy anions. Under these conditions it appears very likely that the  $\text{MgO}$  surface is indeed negatively charged below 800 K. It attracts the solute carbon species which are either  $\text{CO}_2^{2-}$  or  $\text{CO}^-$ , i.e., carbon atoms bonded to one or two  $\text{O}^-$  states,<sup>13,14</sup> hence positively charged defects in the  $\text{MgO}$  structure. The very pronounced temperature-dependent changes of the subsurface carbon concentration profiles reported earlier,<sup>13</sup> as well as the

strange CO<sub>2</sub> gas evolution kinetics,<sup>36</sup> suggest that the surface charge and the reversal of polarity which occurs near or above 800 K are important factors in controlling the subsurface diffusion of carbon impurities and their surface reactivity.

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