PHYSICAL REVIEW B VOLUME 50, NUMBER 7 15 AUGUST 1994-I

Bond ionicity of alkaline-earth oxides studied by low-energy D^+ scattering

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(Received 9 February 1994; revised manuscript received 25 April 1994)

Low-energy D^+ scattering is employed to explore the nature of the bonding of polycrystalline alkaline-earth oxides MgO, CaO, SrO, and BaO, with particular emphasis on the investigation of the ionicity of the topmost-layer atoms. Increasing ionicity as one goes to the heavier cations is concluded from the probability of the resonance neutraliztion of the D^+ ions, which is consistent with the conventional chemical arguments based on electronegativity scales but is in apparent contradiction to the results of recent *ab initio* cluster-model calculations. It is also concluded that the metallic Ba layer is formed rather patchily on the BaO surface after the heat treatment up to 1000 °C. This is probably because free Ba atoms, being supplied by the reaction of BaO with the Ta substrate, are precipitated at the BaO surface. Another example is concerned with the interactions of the Ba adatoms with Si(001) and Pt(111) surfaces; Ba is found to have marked covalency with the substrate atoms.

I. INTRODUCTION

Interest in the electronic properties of narrow-band metal oxides has recently been stimulated by the discovery of high-T_c superconductors. The unique conductivity behavior of undoped oxides as ionic insulators and to a certain extent as metallic conductors has been qualitatively explained on the basis of the framework developed by Zaanen, Sawatzky, and Allen (ZSA).[1-3] However, the chemical argument concerning ionicity, covalency, and polarization in the metal-oxygen interactions is still rather controversial. The formal oxidation state may have little significance in describing the real charges of the ions because of the orbital hybridization. Even if the complete charge distribution of a crystal were determined precisely, one would still need a prescription for decomposing the total charge into component atoms. To circumvent this difficulty, many different attempts have been made to formulate the ionicity from the existing experimental data such as thermodynamic values, interband energies, and dielectric constants.[4-7] Despite a considerable research effort, ionicity even of simple alkaline-earth (AE) oxides is still under significant debate: The argument based on electronegativity scales[7] suggests that the ionic character increases along the series MgO, CaO, SrO, and BaO. Very recently, however, the purely ionic model in the ZSA framework is shown to be very applicable to the AE oxides.[2] This picture has been refined by cluster-model calculations using a variety of *ab initio* wave functions and some degree of covalency is concluded for the heavier AE oxides.[8-10] The increasing covalent character going from MgO to BaO may be related to (a) the low-lying empty *d* orbitals of the metal cations which may contribute to the covalent bonding with oxygen, and (b) the instability of the O^{2-} ions due to the smaller Madelung potential of the heavier oxides. Similar conflicts are seen in many aspects of solid-state physics,[11,12] and the controversies basically come from a lack of the unified way to rationalize this kind of issue. Very recently, we have developed an experimental approach for the straightforward investigation of the bond ionicity without any sophisticated assumptions.[13-16] In this paper, we apply it to the bond nature analysis of the AE oxides.

This technique rests on the experimental fact that the electron-capture probability of very slow (~ 100 eV) deuterons (protons) scattered from solid surfaces is dependent upon the ionicity of individual target atoms:[13,16] D^+ survives neutralization considerably in scattering from perfectly ionic compounds such as alkali halides, whereas almost complete neutralization occurs for D^+ scattered from materials with metallic or covalent orbital hybridization. It is well established that ions can capture an electron via one-electron resonance neutralization (RN) and two-electron Auger neutralization (AN). This is in fact the case for D^+ scattering. However, AN should not lead to such a remarkable chemical effect. This feature comes from RN characteristic of D^+ as schematically shown in Fig. 1:[17] The D 1*s* level, located just around the bottom of the valence band, is promoted in the vicinity of a surface due to the image charge effect and the antibonding interaction with a target core orbital and, hence, the resonance condition is satisfied energetically with the band. The neutralization probability is determined by the competition between the duration of ion surface interactions ($\sim 10^{-15}$ sec) and the lifetime of the D 1*s* hole at a surface. The hole diffuses irreversibly into the band if target atoms have metallic or covalent orbital hybridization, but hole diffusion is suppressed if the target is perfectly ionized. Thus, the probability of RN ($D^+ \rightarrow D^0$), being associated with the mobility of the hole (electron) from the target into the ligands, provides an experimental definition of bond ionicity, which has not been achieved by most of the alternative approaches. This technique has been successfully applied to the charge state analysis of the alkali-metal adatoms on transition metal and semiconductor surfaces.[14-16]

II. EXPERIMENT

The experiments were made in an ultrahigh vacuum (UHV) chamber (base pressure of 1×10^{-8} Pa) equipped

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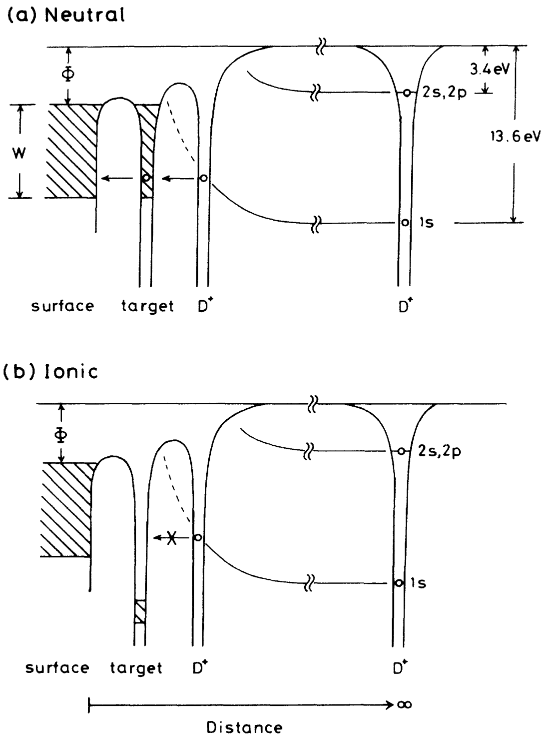

FIG. 1. Schematic views of energy-level diagram for resonance neutralization of D^+, associated with ionic level promotion and subsequent hole diffusion into the band. (a) The D 1*s* hole diffuses into the band irreversibly via the intermediate target-hole state if the target has covalent or metallic orbital hybridization with the ligands, while (b) the hole diffusion is suppressed if the bonding is perfectly ionic.

with facilities for low-energy ion scattering (LEIS), Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS), and a load-lock system for sample transfer. The He^+ and D^+ ions were generated in a discharge-type ion source and were mass analyzed by a Wien filter. The ion source was attached to the sample chamber through three differentially pumped vacuum chambers containing lens systems. The D^+ and He^+ ions with kinetic energy E_0 ranging from 100 eV to 1 keV were incident upon a surface with an angle of 80° from the surface and were scattered with a laboratory scattering angle of 160°. They were detected by means of a hemispherical electrostatic energy analyzer with a constant energy resolution of 1 eV.

The samples of BaO, SrO, CaO, and MgO were polycrystalline films prepared by thermal decomposition of corresponding carbonates or nitrates:[18] The powders of $BaCO_3$ or $SrCO_3$ were coated on a Ta sheet with a thickness of ~ 100 μm with the aid of a nitrocellulose binder and decomposed in vacuum by heating at about 1000 °C. During this procedure, the vacuum was degraded to 1×10^{-3} Pa. The measurements were started when the background pressure was reduced below 1×10^{-7} Pa. These samples showed no traces of carbon in AES. The ion beam bombardment yielded no charging effects since the reaction of BaO (SrO) with the Ta substrate provided isolated Ba (Sr) atoms in the bulk of BaO (SrO) and the sample became a *n*-type semiconductor.[19] On the other hand, CaO and MgO prepared with this procedure showed tremendous charging due to the ion beam bombardment probably because no such reactions occur at the interface. So, we prepared CaO and MgO in another way: $Ca(NO_3)_2$ and $x\mathrm{MgO}\cdot y\mathrm{Mg(NO_3)_2}\cdot z\mathrm{H_2O}$ ($x=1$–3, $y=1,2$, $z=5,11$) were initially precipitated on a Pt foil from aqueous solutions of $Ca(NO_3)_2\cdot 6H_2O$ and $Mg(NO_3)_2\cdot 6H_2O$, respectively, and then were decomposed in air by resistive heating of the foil at about 700 °C. The samples were immediately inserted into the UHV chamber and cleaned by heating at about 1000 °C. The grains of these films were so fine that the charging effect was successfully suppressed by heating them up to 800 °C during the measurements.

The Si(001) wafer was cleaned by resistive heating in UHV, yielding a sharp two-domain 2×1 pattern in LEED. The Pt(111) surface was prepared with a standard oxygen treatment and exhibited a sharp 1×1 pattern in LEED. The cleanliness of these surfaces was checked by means of LEIS using an $E_0=1$ keV He^+ beam. Ba, as well as Cs, was deposited on these surfaces held at room temperature from carefully outgassed dispensers (SAES Getters, Inc.).

III. RESULTS AND DISCUSSION

In general, ions scattered from the outermost surface layer are more likely to survive neutralization than those scattered from the bulk, and form surface peaks in their energy distribution. This is in fact the case for scattering of rare-gas ions such as He^+ and Ne^+ which is neutralized mainly via AN. In D^+ scattering, however, the appearance of the surface peak is dependent sensitively upon the bond nature of the individual target atoms due to the contribution of RN ($D^+ \rightarrow D^0$) shown in Fig. 1. Among the surfaces of so-called ionic compounds, indeed, the surface peaks are recognized only in the highly ionic case such as alkali halides but are absent for oxides with some covalency like Al_2O_3, SiO_2, and TiO_2 (Refs. 13, 15, and 16). Thus, D^+ scattering is the experimental method that can single out the case of complete ionicity.

A. BaO on Ta

As described in the literature,[18–20] the heat treatment of BaO in UHV makes it semiconducting because the free Ba atoms are provided by the reaction at the interface,

$$6\mathrm{BaO}+\mathrm{Ta}\rightarrow \mathrm{Ba_3TaO_6}+3\mathrm{Ba}\ .$$

The segregation of Ba at the topmost layer may also reduce the surface work function considerably, providing the basis for the application of BaO or its composites to the thermionic emitter. In the present case, the work function was measured to be 2.1 eV from the width of the UPS spectrum. In Fig. 2 is shown the D^+ energy spectrum obtained at the BaO/Ta surface (a) together with the spectral change due to subsequent exposure of 100 L (1 L$=1.3\times10^{-8}$ Pa s) O_2 gas (b). The energies for the

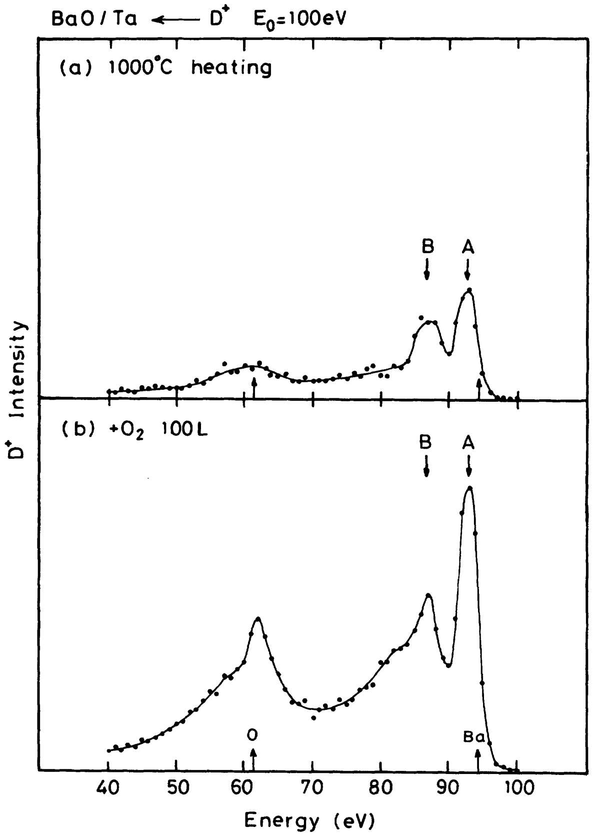

FIG. 2. Energy spectra of $E_0=100$ eV D^+ scattered from polycrystalline BaO on the Ta substrate. The measurements were made for (a) the surface just after the heating in UHV at about 1000 °C, and (b) the surface exposed to 100-L O_2 gas. The energies corresponding to elastic binary collision with individual target atoms are indicated by arrows on the abscissa.

ideal binary collision of D^+ with individual target atoms are indicated by arrows on the abscissa. The spectrum exhibits surface peaks of Ba and O and they are increased in intensity upon oxygenation. The Ba peak is composed not only of elastic peak *A* but also of the energy-loss peak labeled *B*. The spectral features in Fig. 2(b) are characteristic of BaO and the existence of the marked surface peaks is indicative of large ionicity in the Ba-O bond.[13] As regards inelastic scattering, there exist reionization ($D^+ \rightarrow D^0 \rightarrow D^+$) and electron-hole pair excitation beyond the band gap. These two channels give almost similar energy-loss values in the present case, but we have inferred that loss peak *B* is caused by the *e-h* pair excitation from the comparison of the results of BaF_2.[13]

The heat treatment (~ 1000 °C) of the oxygenated surface in UHV reversibly decreases the Ba peak intensity comparable to that shown in Fig. 2(a). This behavior may be concerned with neutralization (metallization) of the surface Ba atoms. On the other hand, the small work function ($\Phi=2.1$ eV) may also be responsible for the occurrence of additional RN to the excited 2*s* or 2*p* state of D^+ ($D^+ \rightarrow D^*$; see Fig. 1). The latter process is in fact observed at alkalated surfaces as a steep drop of the surface peak intensity at the work function values of 3–3.5 eV.[14] However, the opening of this channel is known to be delayed considerably for *n*-type semiconductor surfaces with a large band gap like $TiO_2(110)$ ($E_g=3.0$ eV).[15] The same is essentially true for BaO ($E_g=3.8$ eV) where the top of the valence band (mostly with the O 2*p* character) should be located far below the position of the excited 2*s* and 2*p* states of D^+ even when the work function goes down to 2.1 eV. In this case, RN to both ground state ($D^+ \rightarrow D^0$) and excited state ($D^+ \rightarrow D^*$) occurs simultaneously provided that the 6*s* state of the surface Ba atoms (usually an empty conduction-band state) is in part occupied or, in other words, the metallization of the surface occurs. Indeed, D^+ is neutralized almost completely at the Ba-metal surface.[13] The remaining intensity in Fig. 2(a) shows that such a metallic layer is formed rather patchily on the BaO surface.

B. Ba on Si(001) and Pt(111)

In the context of the above discussion, interest may also extend to the bond nature of Ba on various solid surfaces other than BaO. In order to avoid complexity coming from RN ($D^+ \rightarrow D^*$), we focus here only on a low Ba coverage case showing the work function above 3.4 eV. Figure 3(a) exhibits the D^+ energy spectra obtained at the Ba-adsorbed Si(001) surface (a solid line) and the spectral change due to successive 2-L O_2 exposure (a broken line). Also shown in Fig. 3(b) for reference purposes

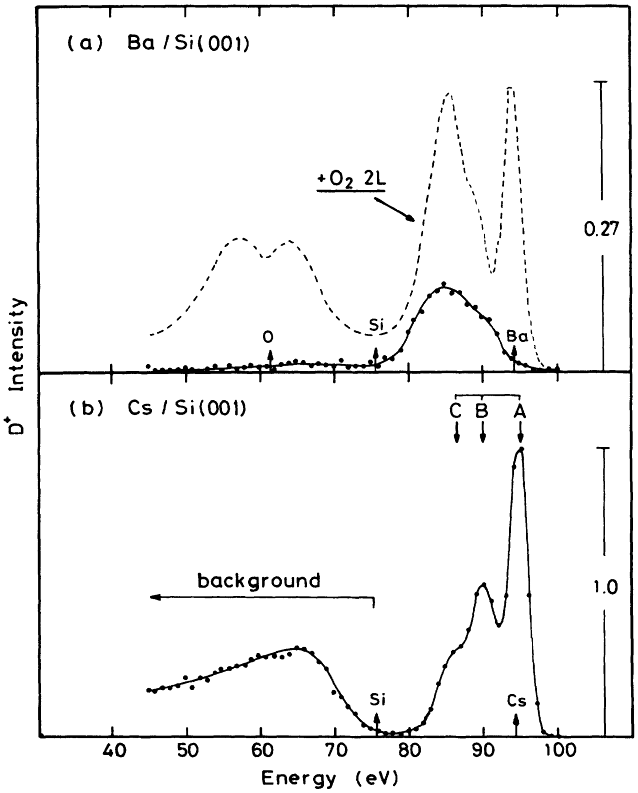

FIG. 3. Energy spectra of $E_0=100$ eV D^+ scattered from (a) the Ba-adsorbed Si(001) surface and (b) the Cs-adsorbed Si(001) surface. Both surfaces exhibit the same work function of 3.8 eV. The spectra are normalized in intensity relative to the Cs surface peak.

is the D^+ energy spectrum for the Cs-adsorbed Si(001) surface where Cs is known to be perfectly ionized.[16] Ba and Cs were deposited so that the work function of the surface was reduced from 4.9 to the same value of 3.8 eV. The amount of Cs deposited is estimated to be 1.0×10^{14} adatoms/cm^2 from this work-function value though the absolute value of the Ba coverage is not determined. Since the D^+ ions are perfectly neutralized at the clean Si(001) surface, the spectra in Fig. 3 are related to the existence of the adatoms. The spectral intensities are normalized relative to the Cs peak intensity. The Ba peak is composed mostly of the inelastically scattered D^+ ions. The elastic peak emerges upon oxygenation though it is rather small in intensity compared to the Cs peak shown in Fig. 3(b). These observations indicate that Ba is essentially neutral on the Si(001) surface and oxygenation ionizes the Ba adatoms only in part.

The origin of the spectral structures appearing in Fig. 3(b) has been revealed in the literature;[16] peaks *B* and *C* are due to *e-h* pair excitation (Si $sp^3 \rightarrow$ Cs 6*s*) and reionization ($D^+ \rightarrow D^0 \rightarrow D^+$), respectively, occurring in a single collision with the Cs adatom, while the broad spectral background appearing in the energy range below 75 eV is due to multiple scattering involving the substrate Si surface and is caused by reionization of neutralized D^0 during collision with the Cs adatoms just before leaving the surface. On this basis, the loss peak for Ba shown in Fig. 3(a) is energetically assignable to reionization and, at the oxygenated surface, it is also contributed to by the loss peak due to *e-h* pair excitation (O $2p \rightarrow$ Ba 6*s*). The structure below $E=75$ eV at the oxygenated surface is attributed to the background overlapping with the O surface peak.

A similar investigation is made at the Pt(111) surface and the results are shown in Fig. 4; Ba is deposited with the same amount as in Fig. 3(a), the intensities being normalized relative to the Cs peak in Fig. 3(b). The spectrum is composed of the background due to reionization and no appreciable surface peak emerges. The same spectral features are observed at the Cs-, O-, and CO-adsorbed Pt(111) surfaces. The Ba peak is not increased even after oxygenation though the O peak becomes distinguishable. These results show that the Ba adatom is not ionized on the Pt(111) surface, and that the ionic interaction between Ba and coadsorbed O is rather weak on Pt(111) compared to that on Si(001).

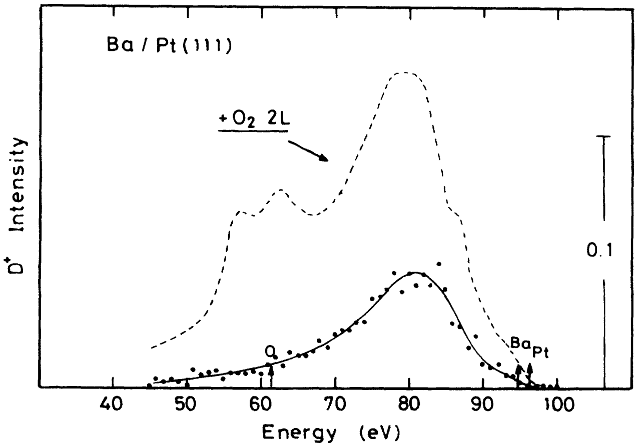

FIG. 4. Energy spectra of $E_0=100$ eV D^+ scattered from the Ba-adsorbed Pt(111) surface. The amount of Ba adatoms is the same as in Fig. 3(a) and the intensity is normalized relative to the Cs peak in Fig. 3(b).

C. SrO, CaO, and MgO

Figure 5 shows energy spectra of the $E_0=100$ eV D^+ ions scattered from (a) SrO, (b) CaO, and (c) MgO. The cationic surface peak decreases in intensity relative to the O peak in going from SrO to MgO. SrO becomes semiconducting due to the reaction similar to the BaO/Ta case, but metallization of the surface is not strongly concluded. The spectrum for MgO has a small peak around $E=80$ eV resulting from the Ca atoms segregated from the bulk,[21] and the Mg peak can be overlapped with the loss peak *B* for Ca. The separation of these two components is made by increasing the kinetic energy of D^+; the spectrum for the $E_0=200$ eV D^+ ions is shown in Fig. 6 together with the result for CaO. The Mg peak is

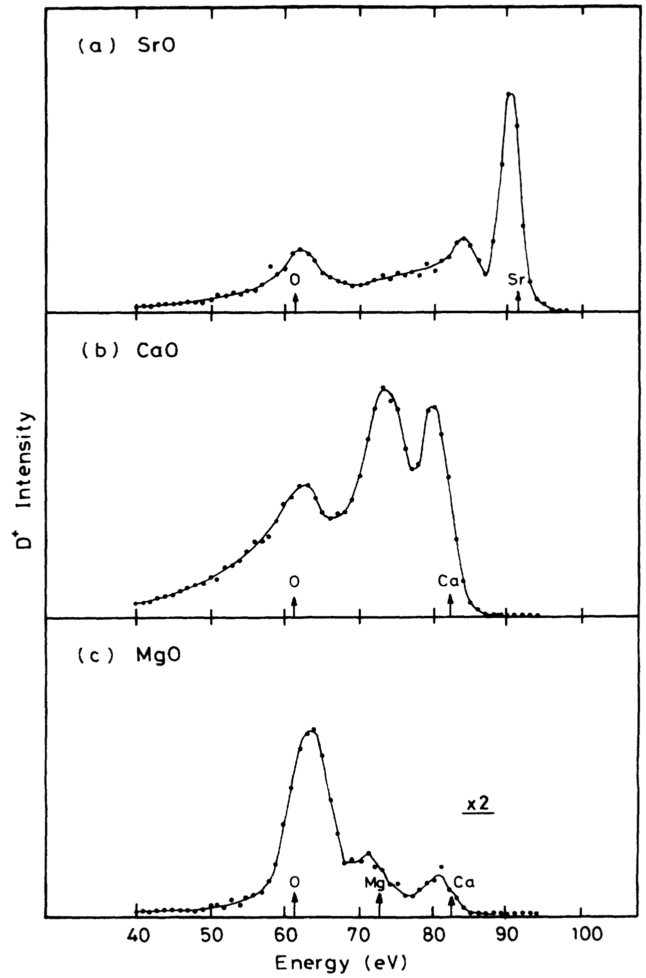

FIG. 5. Energy spectra of $E_0=100$ eV D^+ scattered from the polycrystalline surfaces of (a) SrO/Ta, (b) CaO/Pt, and (c) MgO/Pt.

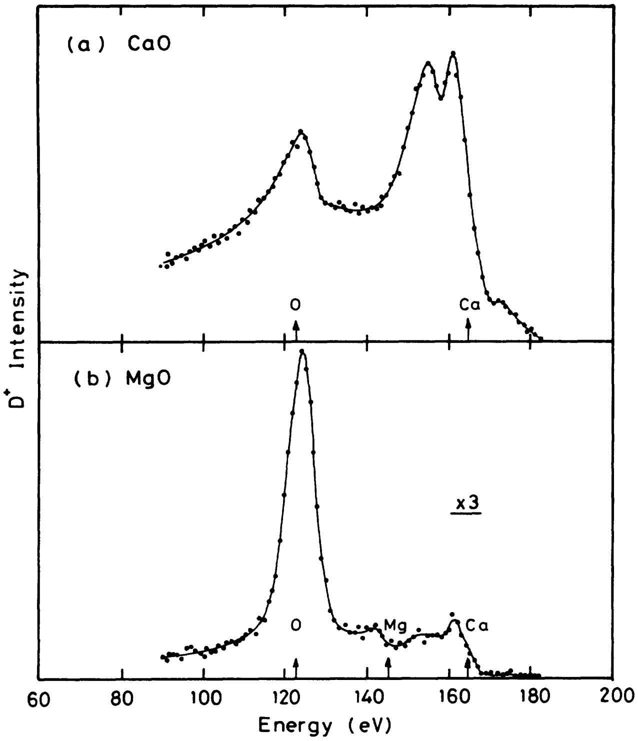

FIG. 6. Energy spectra of $E_0 = 200$ eV D$^+$ scattered from the polycrystalline (a) CaO and (b) MgO surfaces.

rather small in intensity compared to the Ca peak. This result does not necessarily mean that the Mg atom is missing at the topmost layer. Typically shown in Fig. 7 is the energy spectrum of He$^+$ ($E_0 = 1$ keV) scattered from the same surface. The surface peaks for O, Mg, and Ca atoms are clearly recognized in He$^+$ scattering though they are shifted towards the higher-energy side due to the charging effect. The surface is thus found to be composed of MgO with a small amount of the segregated Ca ions. The grains of MgO are thought to be surrounded mostly by the neutral (001) face where Ca, being substituted for Mg, protrudes by 0.4±0.1 Å from the ordinary MgO plane because of the large ionic radius of Ca^{2+} compared to Mg^{2+}.[21] The marked contrast in the appearance of the Mg surface peaks between D$^+$ and He$^+$ scattering can be ascribed to the contribution of RN (D$^+ \rightarrow$D^0) and, therefore, the Mg-O bond is concluded to have covalency to some extent. On the other hand, the O peak appears with considerable intensity in the D$^+$ spectra despite nearly complete absence of the Mg peak. It is suggested that the broadest valence-band width of MgO relative to the other AE oxides is a result of the direct overlapping of the oxygen orbitals due to a small lattice constant rather than the existence of marked covalency in the Mg-O bond.[10] In any case, the presence of the O peak implies that the hole diffusion via both O-Mg-O and O-O paths is not significant. The bottleneck of hole diffusion from oxygen may be ascribed to the formation of a surface molecule (D$^+$-O^{2-}).[17,22]

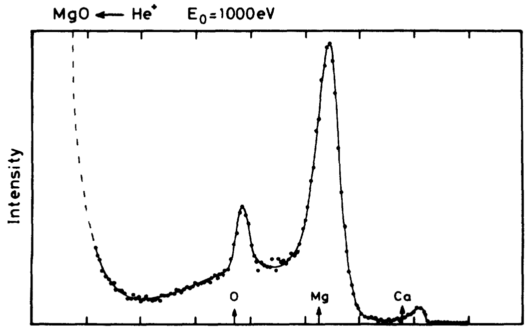

FIG. 7. Energy spectra of $E_0 = 1$ keV He$^+$ scattered from the polycrystalline MgO surface.

The results of D$^+$ scattering indicate that ionicity decreases from SrO through CaO to MgO. This trend is consistent with the chemical argument based on the electronegativity scales:[5–7] In the framework of the dispersion theory, Phillips[7] has proposed a possible measure of bond ionicity f_i as

$$f_i = C^2/E_g^2 ,$$

$$E_g^2 = (E_h^2 + C^2) ,$$

where E_g is the average band gap and E_h and C are referred to as covalent and ionic energy gaps, respectively. The parameters of E_h and C are derived from dielectric constants using complicated assumptions. Briefly, E_h is evaluated from a simple one-gap energy-band model of isotropic group-IV semiconductors with diamond-type structure. Knowing E_h of the elements belonging to the same rows of the Periodic Table, one can estimate the C value from the dielectric constant of the individual heteropolar crystals. In this way, the value of f_i is determined as 0.841, 0.913, and 0.926, respectively, for MgO, CaO, and SrO.

On the other hand, the recent cluster-model calculations[8–10] are in direct conflict with this conventional view and it is claimed that a covalent character increases as one goes from MgO to BaO. These calculations conclude that the decrease of the lattice Madelung potential and the involvement of the low-lying d levels of the cations play an important role in the covalent orbital hybridization. MgO is close to being a perfect ionic crystal with a Mg charge of +1.95, while the charge of Ca (Sr) in CaO (SrO) is +1.88 (+1.85). The discrepancy between these two approaches implies that the ionicity of the AE oxides is a matter of great delicacy and the accuracy of the results is limited by the validity of the assumptions made.

As regards the present results based on the neutralization of D$^+$, we can infer the ionicity only of the outermost-layer atoms. It is likely that the surface ions are not equivalent to the bulk ions regarding the ionicity or the bond character since the electrostatic field at a surface should be largely different from the bulk values due to, e.g., the reduction of the Madelung potential, the polarization-induced orbital hybridization, and ionic charge redistribution. Indeed, the *DV-Xα* calculation of the MgO(001) surface by Satoko, Tsukada, and Adachi[22] reveals that the surface ion is less ionic than the bulk ions because the polarization induces the lowering of the unoccupied Mg 3*s* level and increases the mixing with the occupied 2*p* levels. These effects may act similarly on the surfaces of all the AE oxides so that the increasing ionic character with increase of the cationic masses may hold for the bulk ions as well, though the difference in the ionicity among the bulk AE oxides might be smaller than the surface oxides. In fact, the increasing ionic character along the series of bulk MgO, CaO, SrO, and BaO is obtained from the *DV-X*α calculations using the $[A_{13}O_{14}]^{2-}$ cluster (A = Mg, Ca, Sr, and Ba).[23] Of interest in this respect is the protrusion (~ 0.4 Å) of the Ca ions segregated at the MgO(001) surface. There is an indication[22] that the electrostatic potential decreases rapidly along the direction perpendicular to the surface, so that the charge state of the Ca segregants might be different from the Ca ions at the flat CaO surface. This effect, however, is not explicitly observed in the present investigations.

IV. SUMMARY AND CONCLUSIONS

In this work, we have presented an experimental approach to studying the ionicity of the alkaline-earth oxides. On the basis of resonance neutralization ($D^+ \rightarrow D^0$) associated with the hole diffusion into the band, the nature of the bonding of the topmost-layer atoms of polycrystalline BaO, SrO, CaO, and MgO has been investigated. The increasing cationic surface peak intensity relative to the O peak as one goes from MgO to BaO indicates that the bond ionicity increases with increase of the cationic mass. Although the present investigation concerns only the topmost-layer atoms, this trend is inconsistent with the conventional views of the ionicity of the bulk alkaline-earth oxides derived from the electronegativity arguments, but is apparently incompatible with the results of recent cluster-model calculations. The decreasing electrostatic potential at the surface has only a marginal effect on the neutralization probability of D^+ as manifested by the appearance of the Ca surface peaks at both CaO and Ca-segregated MgO surfaces despite the protrusion of the Ca ions at the latter surface. The heating of BaO on the Ta substrate leads to the formation of the patches of the metallic Ba layer which may be responsible for utilizing BaO and its composites as a thermionic emitter. The interaction of Ba with the clean Si(001) and Pt(111) surfaces is also investigated and the Ba-Si and Ba-Pt bond is concluded to have marked covalency compared to the Cs-Si or Ba-O bond.

ACKNOWLEDGMENTS

We are grateful to K. Era for fruitful conversations. Special thanks are due to B. Tilley for enlightening discussions and a critical reading of the manuscript. This work was supported in part by the Special Coordination Funds Promoting for Science and Technology.

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