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Determination of bond ionicity using low-energy D^+ scattering

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We report on the systematic investigation of neutralization of low-energy D^+ ions scattered from 17 ionic-compound surfaces with particular emphasis on the relation between the neutralization probability of D^+ and the ionicity of the surface atomic bonds. The D^+ ions tend to survive neutralization provided that the target atom is completely ionized, whereas almost complete neutralization results if the target has covalent or metallic orbital hybridization with the ligand. The D^+ spectra from nitrates, sulfates, and carbonates of Na and K, as well as K_2SiO_3, exhibit surface peaks of D^+ surviving neutralization for both cations and oxygen, indicating large ionicity in the alkali-metal–oxygen bond. Rather exceptional is Na_2SiO_3, for which a relatively small ionicity is concluded from the absence of surface peaks. For the alkaline-earth compounds, ionicity decreases in going to the light elements as evidenced by the decrease of the surface-peak intensity. The occurrence of charge-exchange relaxation between cations and anions of $NiSO_4$ and $CuSO_4$ results in large neutralization probability of D^+, while the closed-shell structures of Ag^+ ($4d^{10}$) and Pb^{2+} ($6s^2$) in $AgNO_3$ and $Pb(NO_3)_2$, respectively, suppress neutralization to some extent so that the appreciable surface peaks appear.

I. INTRODUCTION

Electronic transitions between particles and solid surfaces have attracted considerable attention as they constitute one of the most fundamental processes in surface dynamics. Specifically, a comprehensive understanding of such transitions gives insight into molecular dissociation and also is crucial for surface analysis techniques such as low-energy ion scattering (ISS), secondary-ion-mass spectroscopy, and electron stimulated desorption. Considerable research has, therefore, been devoted to this subject.[1-9] It is well established that an electron is captured either via a one-electron resonance neutralization (RN) or a two-electron Auger neutralization (AN), and that the relative role of these processes is sensitively dependent upon the energy position of the vacant ionic level relative to that of the valence band. Alkali-metal ions, having a vacant *s* level close to the Fermi level of the surface, are neutralized mainly via RN. Rare-gas ions, on the other hand, have the ground state well below the bottom of the valence band so that the ion captures a valence electron via AN. As for hydrogen, the ionization energy is just around the middle of these two extremes and neutralization is seemingly quite unique.[10,11] The H^+ ions are neutralized with a fairly large probability on metal surfaces, whereas alkali-metal or rare-gas ions tend to survive neutralization with such surfaces. The unique behavior of H^+ arises from the H 1*s* level being located near the bottom of the valence band. As sketched in Fig. 1(a), the resonance condition is satisfied between the 1*s* level and the band, because the 1*s* level can be promoted in the vicinity of a surface due to the image-charge effect and the antibonding interaction with a target core orbital.[3,4,12] This process should provide a striking contrast to RN of the alkali-metal ions where the ionic levels are rather shallow. The neutralization probability of H^+, in fact, is determined by the competition between the duration of the ion-surface interaction ($\sim 10^{-15}$ s) and the lifetime τ ($\tau = \hbar/W$) of the electron or the hole in the valence band (with a width of W).[12]

It is notable that the ion-surface interaction should indeed have a local character in hard collision besides the interaction with the continuum of the conduction electrons. This particular effect is, in fact, anticipated, in backscattering of H^+ and D^+ ions due to the small spatial extent of the 1*s* orbital (~ 0.5 Å). Accordingly, as shown in Figs. 1(a) and 1(b), the above-mentioned band picture of RN can, as an alternative, be described as involving an ionic hole, which diffuses irreversibly if target atoms bond to ligands via metallic or covalent orbital hybridization but does not diffuse if the bonding is ionic. We have reached this conclusion on the basis of a large number of D^+ scattering experiments,[13] in which D^+ survives neutralization considerably in scattering from simple ionic compounds, such as alkali halides, while nearly perfect neutralization occurs in scattering from metals and covalent semiconductors. Thus, resonance neutralization of the D^+ ions provides an experimental definition of ionicity in surface atomic bonds. In addition to this aspect, D^+ can excite the electron-hole pair during collision. From the energy loss value of this channel, further information about the bond nature can be obtained.[13] We have successfully applied this framework to the chemical analysis of alkali-metal and alkali-halide adatoms on metal and semiconductor surfaces.[14,15] In this paper, we report on the systematic investigation of D^+ scattering from some ionic compounds with particular emphasis on the discussion of ionicity of individual target atoms.

II. EXPERIMENT

The experiments were made in an ultrahigh vacuum (UHV) chamber equipped with facilities for ISS, ultra-

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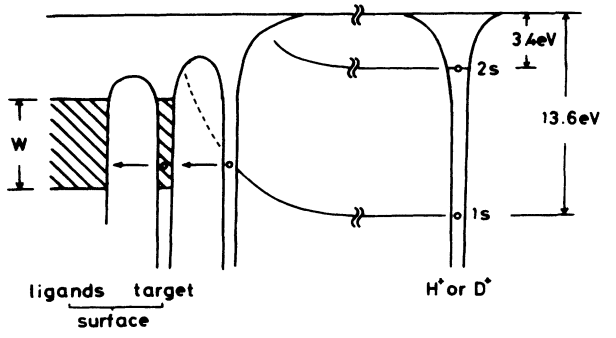
(a) Neutral



(b) Ionic

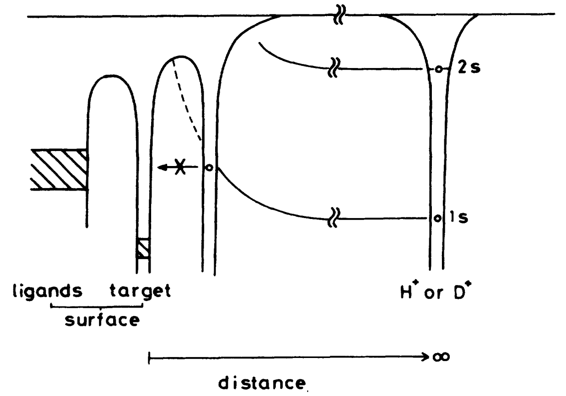


FIG. 1. Energy-level diagram for resonance neutralization of H^+ or D^+ ions associated with a promotion of the 1s level in the vicinity of a surface followed by diffusion of the hole into the band.

violet photoelectron spectroscopy, low-energy electron diffraction (LEED), and a load-lock system for sample transfer. The He^+ and D^+ ions were generated in a discharge-type ion source and were then 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 ion dose in each measurement was restricted to below 3×10^{13} ions/cm^2 in order to minimize surface decomposition.

In the present work, measurements were made for the following 17 samples: $SrTiO_3$, $NaNO_3$, KNO_3, Na_2SO_4, K_2SO_4, Na_2CO_3, K_2CO_3, Na_2SiO_3, K_2SiO_3, $Ca(NO_3)_2$, $Sr(NO_3)_2$, Al_2O_3, $Al_2(SO_4)_3$, $NiSO_4$, $CuSO_4$, $AgNO_3$, and $Pb(NO_3)_2$. The Nb-doped *n*-type $SrTiO_3(100)$ surface was cleaned in UHV by repeated Ar^+-ion bombardment followed by annealing at 900 °C, yielding a sharp 1×1 LEED pattern. The other samples, except for Al_2O_3, were soluble in water and anhydrous salts could be precipitated on a Ta sheet by heating them in air at 200 °C. The samples were immediately inserted in the UHV chamber via the interlock system. Before the measurements, the samples were dehydrated again (~300 °C) by heating the Ta filament placed just behind them, which also was used to suppress the charging effect during the ion-beam bombardment. This treatment might not achieve the complete cleanliness of the surface. One of the likely contaminants was hydrocarbon, but it should not have significant contribution to D^+ scattering because of preferential neutralization. Indeed, we confirmed that some of the alkali-halide samples (KI,NaBr) obtained with this procedure gave essentially the same results for thin films *in situ* evaporated in UHV and no traces of oxygen and carbon were recognized in the D^+ spectra. Al_2O_3 (γ alumina) was prepared such that the basic salt $[4Al_2O_3\cdot3N_2O_3\cdot14H_2O]$ precipitated from a solution of $Al(NO_3)_3\cdot9H_2O$ was decomposed in air by heating at 400 °C.

III. RESULTS AND DISCUSSION

A. $SrTiO_3(100)$

Figure 2 shows representative energy spectra of D^+ scattered from the (100) surface of $SrTiO_3$; the measurements were made using a D^+ beam of (a) 100 eV, (b) 200

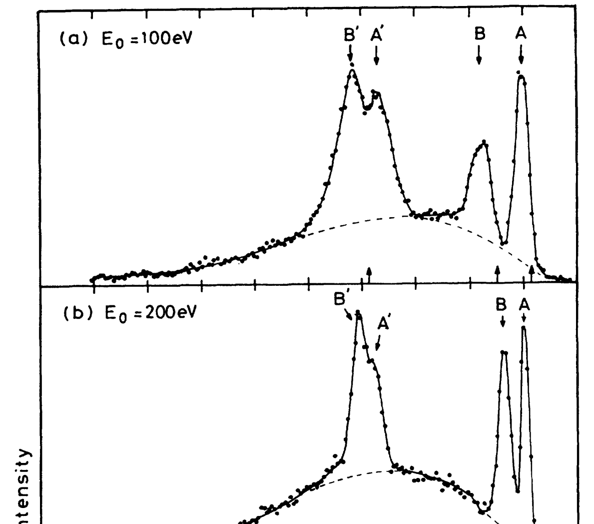


FIG. 2. Energy spectra of D^+ scattered from the $SrTiO_3(100)$ surface measured using a D^+ beam of (a) 100 eV, (b) 200 eV, and (c) 500 eV. The energies corresponding to the elastic binary collision with individual target atoms are shown by arrows with chemical symbols on the abscissa.

eV, and (c) 500 eV. The energy position of ideal elastic binary collision with each surface component is indicated by an arrow on the abscissa. The spectra are characterized by sharp surface peaks for Sr and O, together with an extended background appearing under the surface peak (indicated by broken lines). The surface peaks are seen to have two components, *A* and *B* for Sr and *A'* and *B'* for O, though the separation of the components, especially for oxygen, becomes less marked as the ion energy increases. As has already been shown in the literature,[13,14] the surface peaks arise from the D^+ ions surviving neutralization in a single collision with the specific target atoms, and constituent peaks *A* (*A'*) and *B* (*B'*) are referred to as elastic scattering and inelastic scattering, respectively. On the other hand, the background cannot be ascribed to surface scattering with a single head-on collision but arises from multiple scattering including deeper layers. We have assigned the background to reionization of once neutralized D^+ ions (D^0) on the basis of the experiment using both D^+ and D^0 beams.[13] Reionization occurs in a small-angle collision between a surface atom and D^0 emerging from the bulk just before leaving the surface. Thus, the yield of the surface peaks rather than the background should be relevant to a discussion of ion neutralization.

As is typically seen in Fig. 2, the surface peaks for constituent atoms are well separated energetically with an increase of the kinetic energy. Here, it should be noticed that the surface peak for Ti is absent, as clearly seen in Fig. 2(c). This does not necessarily mean that the Ti atom is missing at the topmost layer, because the Ti peak is clearly recognized in the energy spectra of scattered He^+ shown in Fig. 3. So, the marked target dependence seen in the appearance of the surface peak is best understood by the effect of ion neutralization. As described in the Introduction, neutralization of D^+ is contributed to by RN while He^+ is neutralized mainly via AN. In He^+ scattering, the surface peaks appear basically for all atoms existing on the topmost surface since the probability of AN is not sensitively affected by the nature of the chemical bond. In D^+ scattering, on the other hand, covalency between Ti and O makes efficient neutralization in D^+-Ti collision. This is equivalent to saying that the valence band has a Ti 3*d* character to a certain extent.[16] On the other hand, RN is largely suppressed in collisions with the almost perfectly ionized Sr atoms and, hence, D^+ tends to survive neutralization.

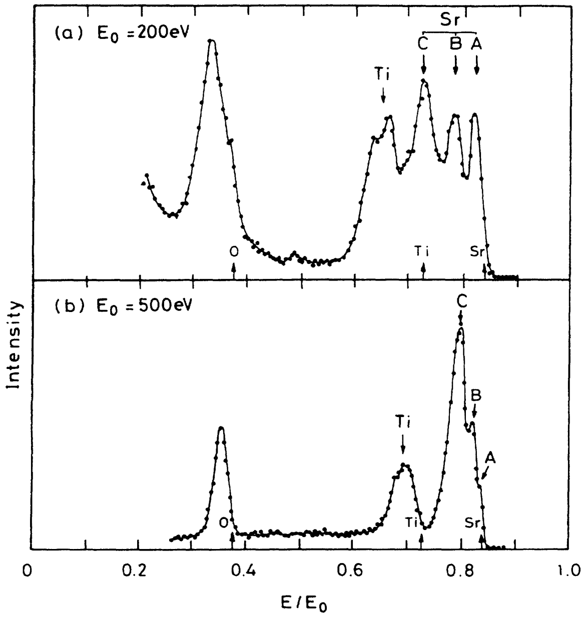


FIG. 3. Energy spectra of He^+ scattered from the $SrTiO_3(100)$ surface using a He^+ beam of (a) 200 eV and (b) 500 eV.

In Fig. 2, the surface peak for oxygen is composed of the elastic peak *A'* and the inelastic peak *B'*. Before further discussion of this structure, it is helpful to see the spectral features of simpler ionic compounds: The O peak in the spectrum of $TiO_2(110)$ is composed mostly of the loss peak (corresponding to peak *B'* in Fig. 2)[15] while, in the spectrum of BaO, peak *A'* has the dominant contribution to the O peak.[13] The spectrum for $SrTiO_3$ is just a compromise between them. From the fact that TiO_2 has marked covalency in Ti-O bonds[16] while the Ba-O bond is highly ionic, it is inferred that the presence of the elastic peak *A'* for oxygen is correlated to the bond ionicity. This is, in fact, manifested by the experimental results shown in the following sections.

As regards inelastic scattering, there exist at least two channels,[13] one being *e-h* pair excitation at a surface and the other being reionization of D^0 neutralized on the incoming trajectory. These processes occur in hard collision, so that the local electronic states around the specific target atoms should be involved.[13] In Fig. 2, peak *B'* is attributed to *e-h* pair excitation. It should be noticed that the energy loss value for O (~ 4.5 eV) is small compared to that for Sr (~ 7.5 eV). This result is understandable on the basis of the local atomic structure as well as the band structure schematically shown in Fig. 4. An O 2*p* electron can be transferred to the Ti 3*d* state during D^+-O collision, whereas it should be excited to the Sr 5*s* state if D^+ collides with Sr. In Fig. 2, the energy-loss value of peak *B'* for O, though not exactly equal to the band-gap energy of $SrTiO_3$ (~ 3.4 eV), may be assignable to the electronic transition between the maximum densities of states. In He^+ scattering shown in Fig. 3, on the other hand, the Sr peak is composed of three peaks, *A*, *B*, and *C*,[12] and the loss peaks *B* and *C* are fairly large in intensity relative to the elastic peak *A*. Peak *B*, identical to that in D^+ scattering, is due to valence electronic excitation while peak *C* can be ascribed to excitation of a Sr 4*p* core electron. The absence of peak *C* in D^+ scattering is caused by the energy position of the 1*s* level being shallower than that of the Sr 4*p* state as shown in Fig. 4. This result suggests that electronic excitation occurs in the collisional regime due to the electron promotion mechanism.[17,18]

B. Alkali salts

In the literature,[13] we have reported that the alkali halides except for Li salts yield clear surface peaks for

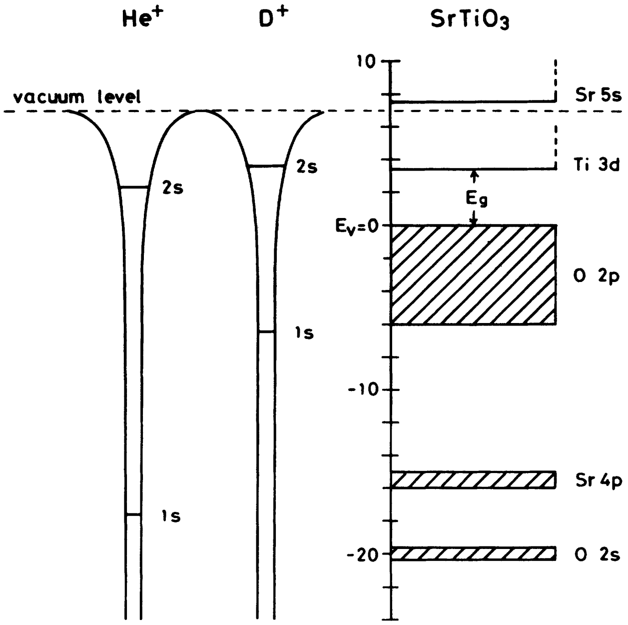


FIG. 4. Schematic views of the band structure of $SrTiO_3$ together with the energy-level diagram of D^+ and He^+ ions.

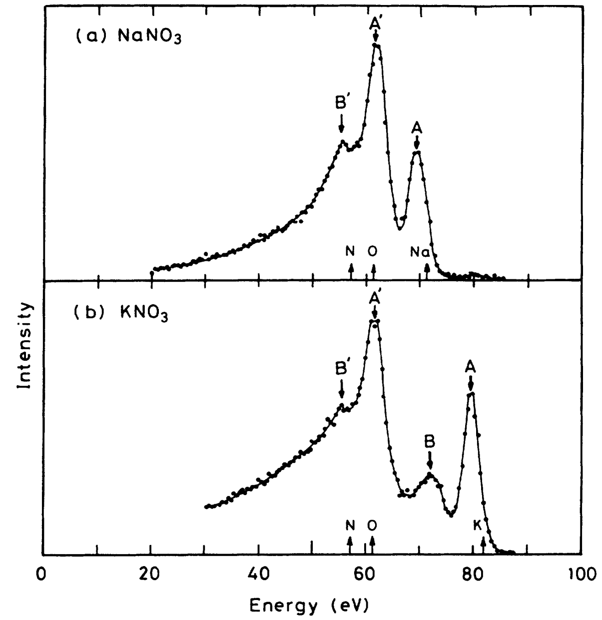


FIG. 5. Energy spectra of D^+ scattered from (a) $NaNO_3$ and (b) KNO_3. The measurements were made using a D^+ beam of 100 eV under the same scattering geometries as in Fig. 2(a). The energies for the elastic binary collision are shown by arrows with chemical symbols on the abscissa.

both cations and anions in the D^+ energy spectra, representing strong ionicity in bonds. The behavior of the lithium halides may not be necessarily interpreted as the existence of covalency in bonds but is assignable to the recoil effect of the light Li atoms by D^+ impact.[19] Indeed, we have confirmed that the Li surface peak, though not clearly recognized in the D^+ spectra, appears with considerable intensity in H^+ scattering where the movement of the recoil Li atom is marginal. As for the other alkali-metal (AM) atoms, the fact that essentially the same result is obtained in H^+ and D^+ scattering shows that the recoil effect can be ignored. In this section, we survey ionicity of the Na and K atoms in the form of nitrates, sulfates, carbonates, and silicates. Shown in Fig. 5 are the D^+ energy spectra ($E_0 = 100$ eV) obtained from (a) $NaNO_3$ and (b) KNO_3. There exist prominent surface peaks (elastic peaks A and A') for constituent atoms except for N. The N peak, if any, might be overlapped with loss peak B' of oxygen. The absence of the N peak is confirmed by increasing the kinetic energy of D^+ as well. As for the O peak, the elastic peak A' considerably exceeds the loss peak B' in intensity.

Figure 6 shows the results for (a) Na_2SO_4 and (b) K_2SO_4. The spectra exhibit surface peaks of all constituent atoms. The S peak (peak A'') in Fig. 6(b) may be overlapped energetically with the K peak (peak A). In the case of carbonates, shown in Figs. 7(a) and 7(b), the surface peaks of Na, K, and O atoms are clearly recognized, though the surface peak for carbon is absent in the spectra, which is confirmed by changing the kinetic energy.

As is seen in Figs. 5-7, since the surface peaks for Na and K (peak A), together with O (peak A'), appear in the D^+ spectra, all of these AM compounds are characterized by highly ionic bonds between AM's and oxygen. However, a major difference exists in the D^+ spectra of the AM silicates, with results as shown in Fig. 8. The surface peaks (peaks A and A') are rather small in intensity compared to the extended background for Na_2SiO_3, whereas marked surface peaks exist for K_2SiO_3. One may think that the remarkable difference between Figs. 8(a) and 8(b) stems from the shadowing effect due to the possible contaminants or the absence of the Na atoms at

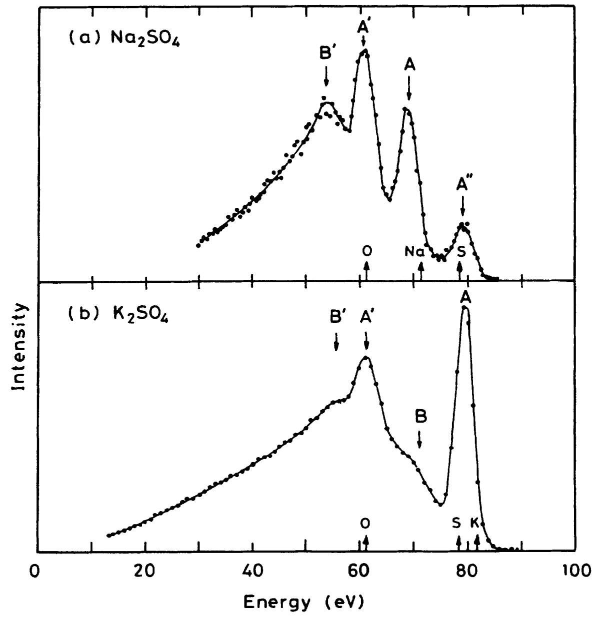


FIG. 6. Same as in Fig. 5 for (a) Na_2SO_4 and (b) K_2SO_4.

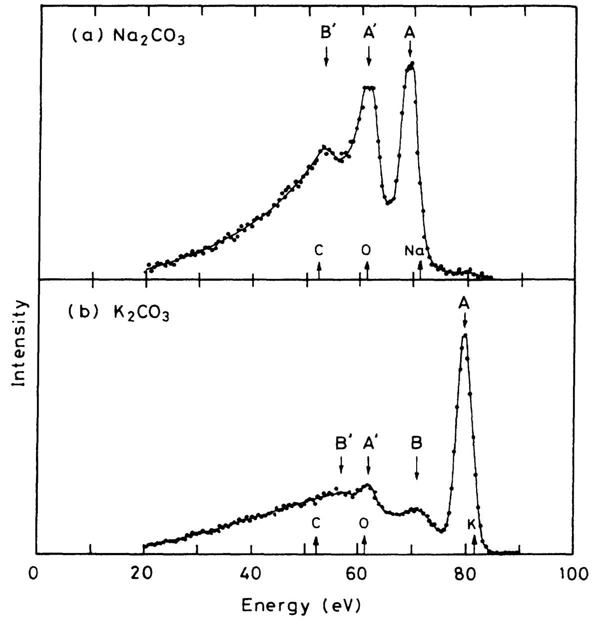


FIG. 7. Same as in Fig. 5 for (a) Na_2CO_3 and (b) K_2CO_3.

the topmost layer. But, this assumption is definitely discarded because a very intense Na peak is observed in the He^+ scattering experiments. Therefore, the absence of intense surface peaks indicates that Na has covalency to some extent in Na_2SiO_3.

The marked contrast between the spectra of Na_2SiO_3 and K_2SiO_3 is attributable either to a large ionization energy of Na (5.1 eV) compared to K (4.3 eV), or to a smaller ionic radius of Na (1.02 Å) than K (1.38 Å). That the ionicity of Na is reduced only for Na_2SiO_3 among the Na salts examined here may be indicative of the small acidity of H_2SiO_3. In this respect, moreover, it has been revealed that small basicity of Na compared to K or Cs leads to specific chemisorptive bonds on semiconductor surfaces.[14,20] The surface peaks exist in the D^+ spectra for the Cs and K adatoms on Si(100), Ge(100), and SiO_2 surfaces, whereas the surface peak is nearly absent for Na on the same substrates. Rather experimental is the $TiO_2(110)$ surface[15] on which surface peaks appear with considerable intensity for Na, K, and Cs adatoms. In these studies, it is concluded that the charge state of AM's is correlated closely either with the microscopic arrangement of surface oxygen atoms[15] or with the existence of active dangling-bond states[14,21] by which the AM's electron can be accommodated.

C. $Ca(NO_3)_2$ and $Sr(NO_3)_2$

The ionization tendency of the alkaline-earth metals is believed to increase with the atomic weight. Besides $SrTiO_3$, described in Sec. III A, we have already reported that heavy alkaline-earth salts, such as BaF_2, BaO, and $SrCl_2$, have significant ionicity as testified by the existence of intense surface peaks in the D^+ spectra.[13] Shown in Fig. 9 are the D^+ spectra ($E_0=100$ eV) from (a) $Ca(NO_3)_2$ and (b) $Sr(NO_3)_2$. The surface peak of Ca is very small relative to the background for $Ca(NO_3)_2$. In the case of $Sr(NO_3)_2$, both Sr and O surface peaks (peaks A and A') are prominent in the spectra and the spectral feature is quite similar to that shown in Fig. 2(a). It is confirmed again that the appearance of the surface peaks for the cations (peak A) and oxygen (peak A') is correlated to each other. These results clearly indicate that ionicity tends to increase in going to the heavier cationic species. A similar tendency is found in the bond ionicity of alkaline-earth oxides MgO, CaO, SrO, and BaO, as well as fluorides MgF_2, CaF_2, SrF_2, and BaF_2.[22]

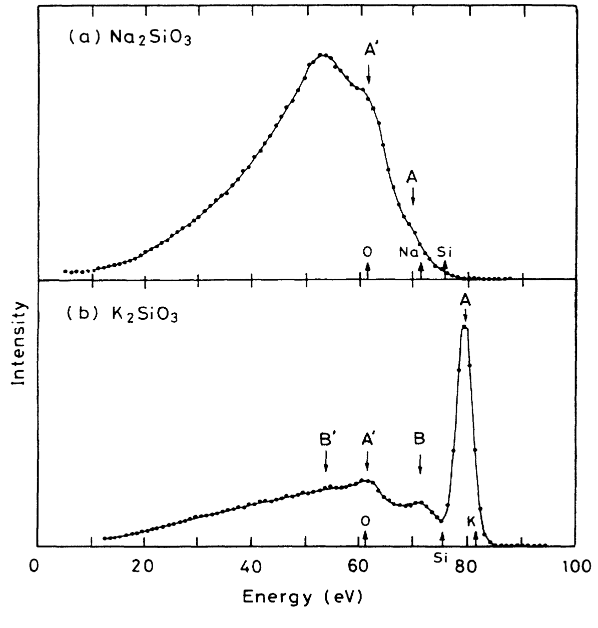


FIG. 8. Same as in Fig. 5 for (a) Na_2SiO_3 and (b) K_2SiO_3.

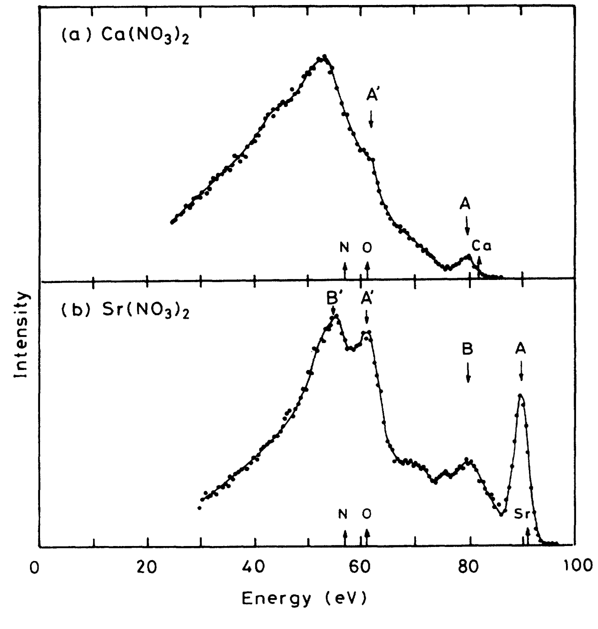


FIG. 9. Same as in Fig. 5 for (a) $Ca(NO_3)_2$ and (b) $Sr(NO_3)_2$.

D. Other ionic compounds

In this section, the oxides of metal elements other than alkali metals or alkaline-earth metals are explored. Typically, shown in Fig. 10, are the D^+ spectra ($E_0=100$ eV) from (a) Al_2O_3 (γ-alumina) and (b) $Al_2(SO_4)_3$. The spectra are characterized by the background due to reionization and no significant surface peaks of constituent atoms appear. This indicates that the bonding is not perfectly ionic and marked contribution of covalency exists in the Al—O bond. It is notable that the S peak is absent for $Al_2(SO_4)_3$ though it appears in the spectra of Na_2SO_4 shown in Fig. 6(a), indicating that the appearance of the S peak is also correlated to the bond ionicity.

As regards transition-metal (TM) oxides, we have already mentioned that TiO_2 and $SrTiO_3$ yields no Ti surface peak because of the hybridization of the Ti $3d$ and O $2p$ orbitals [see Fig. 2(c)]. In the case of the oxides of TM's with more than half-filled d orbitals, on the other hand, the cationic d state is fairly localized due to strong Coulomb interaction.[23,24] Shown in Figs. 11(a) and 11(b) are the D^+ spectra from $NiSO_4$ and $CuSO_4$, respectively. The spectra are composed only of the background without any surface peaks of the components. In these cases, D^+ can capture an electron from Ni^{2+} ($3d^8$) and Cu^{2+} ($3d^9$) but the resulting $3d^7$ and $3d^8$ states, respectively, are highly excited in energy due to the strong correlation of the d electrons. Hence, the subsequent charge transfer can occur immediately between the cation $3d$ and the ligand O $2p$ states because of the covalency or the orbital hybridization.[23,24] Here, one may think that such a charge-transfer relaxation leading to a final hole state in O $2p$ is not necessary for the absence of the surface peaks since the electron can be transferred from the cationic $3d$ states. In reality, however, this is not sufficient for complete neutralization of D^+. In this respect, it is instructive to note the existence of quasiresonant neutralization (QRN) of the He^+ ions,[25,26] where the closed-shell d electron can be resonantly transferred to the He $1s$ state. Then, the electron transferred to He^+ can be returned to the target d state with a considerable probability (~ 0.5), resulting in survival of He^+. Thus, the RN to the isolated electronic state should not lead to complete neutralization of D^+. In order to verify this assumption, we show in Fig. 12 the results of D^+ scattering from (a) $AgNO_3$ and (b) $Pb(NO_3)_2$. The spectra exhibit clear surface peaks for both cations (peak A) and oxygen (peak A'). In this case,

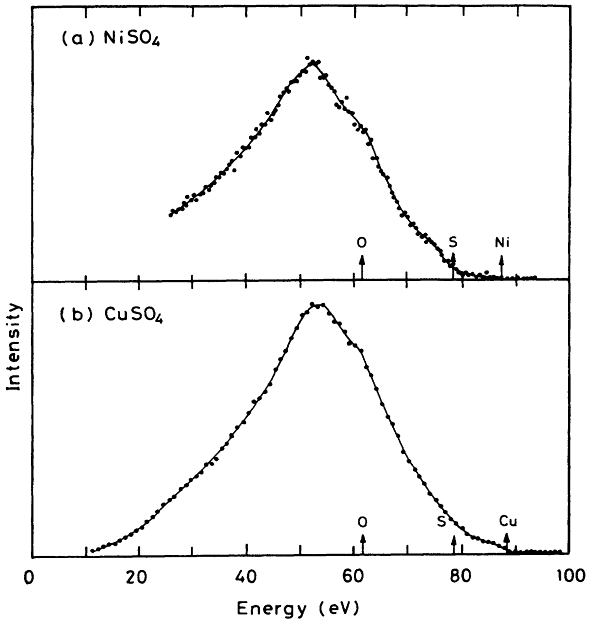


FIG. 11. Same as in Fig. 5 for (a) $NiSO_4$ and (b) $CuSO_4$.

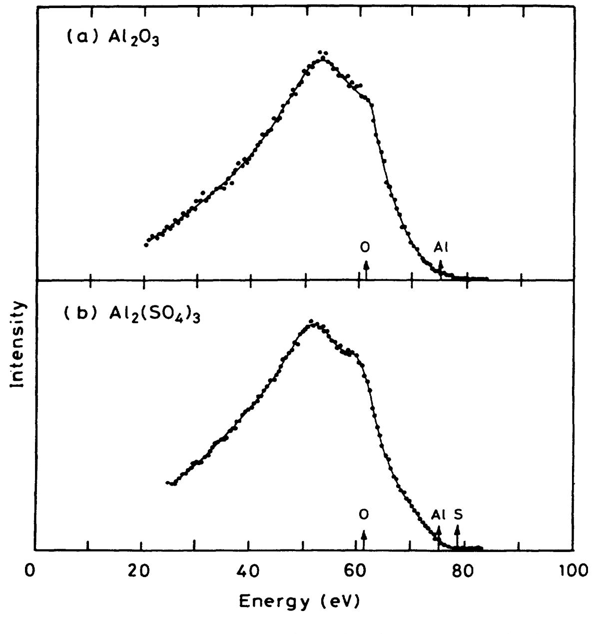


FIG. 10. Same as in Fig. 5 for (a) Al_2O_3 (γ-alumina) and (b) $Al_2(SO_4)_3$.

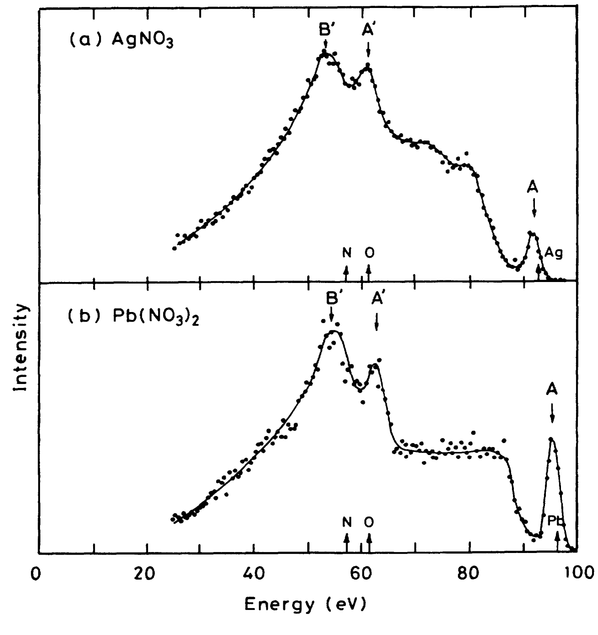


FIG. 12. Same as in Fig. 5 for (a) $AgNO_3$ and (b) $Pb(NO_3)_2$.

the Ag^+ ($4d^{10}$) and Pb^{2+} ($6s^2$) ions have a closed-shell electronic configuration. It is probable that these electronic states satisfy resonance condition with the D 1*s* level without orbital promotion, so that the D^+ ions may suffer QRN to a certain extent. However, the lack of the strong charge-transfer interaction between the cation and oxygen may lead to the presence of the surface peaks in the D^+ spectra.

IV. SUMMARY AND CONCLUSIONS

It is demonstrated that the bonds of solid surfaces can be investigated on the basis of neutralization and inelastic scattering of D^+ ions. The D^+ ions is neutralized nearly completely provided that a target atom has covalency or metallicity with the coordinating atoms, while D^+ tends to survive neutralization when the target atom is ionized. This is because D^+ is neutralized by resonance tunneling of the D 1*s* hole into the target electronic state and subsequent hole diffusion into the ligand electronic state via metallic and covalent orbital hybridization. The survival of neutralization in each binary collision event is estimated from the presence of the corresponding surface peaks in the D^+ energy spectra. The surface peaks of alkali-metal cations, together with the oxygen surface peak, appear in the spectra for nitrates, sulfates, and carbonates of Na and K, indicating strong ionicity in the alkali-metal–oxygen bonds. Rather exceptional is the alkali-metal silicates: the surface peaks are nearly absent for Na_2SiO_3, while the surface peaks for both K and O atoms appear with a considerable intensity in the spectrum of K_2SiO_3. In a series of alkaline-earth salts, it is confirmed that the bond ionicity increases in going to heavier elements. Marked covalency is concluded for the bonding of the Al salts since the surface peaks are completely absent. Further investigation is made for transition-metal and noble-metal salts. The charge-transfer interaction between cations and anions leads to almost complete absence of the surface peaks for $NiSO_4$ and $CuSO_4$, while the isolated, closed-shell structure of Ag^+ ($4d^{10}$) in $AgNO_3$ results in appearance of well-defined surface peaks for both Ag and O. Thus, a true definition of ionicity, which has not been achieved by most of the alternative experimental approaches, appears to be given by the probability of resonance neutralization of D^+.

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