Band effects on neutralization of low-energy D^+ scattering from ionic crystals

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The neutralization of low-energy (< 300 eV) D^+ ions scattered from various ionic compounds such as LiF, $SrCl_2$, LaF_3, PrF_3, SmF_3, TmF_3, ZrO_2, $MnCl_2$, $CoCl_2$, and $CdCl_2$ has been studied in terms of the diffusion of the D $1s$ hole into the anion p band. The surface peak, which is usually absent in the D^+ energy spectra from metallic surfaces, has been clearly observed for each target element except for Mn^{2+} and Co^{2+}. The coupling of the D $1s$ state to the filled p band of LiF and $SrCl_2$ is due mainly to the energy-level-crossing mechanism and the contribution of resonant charge exchange is largely suppressed. Although the D $1s$ hole diffusion into the closed anion p band or the $4f$ state of the rare-earth cations is unremarkable even if the resonant condition is met satisfactorily, the hole diffusion is found to be very much enhanced in D^+ scattering from Mn^{2+} and Co^{2+} because the d state is coupled strongly to both the initial D $1s$ state due to resonant charge exchange and to the final Cl $3p$ state due to covalent hybridization. It is found that the charge-transfer probability is much higher for resonant tunneling than for the energy-level-crossing mechanism.

I. INTRODUCTION

Charge exchange between ions and solid surfaces has attracted considerable attention since it is one of the most important problems of surface dynamics. From the standpoint of practical applications, an understanding of these processes is essential for chemical reaction at surfaces and quantitative surface analyses using low-energy ion-scattering spectroscopy (ISS), secondary-ion mass spectroscopy (SIMS) and electron-stimulated desorption (ESD), and, hence, in the past decade numerous experimental and theoretical studies have been made.[1-12] In terms of ion neutralization, it is commonly recognized that charge capture occurs via both one-electron resonant (RN) and two-electron Auger (AN) processes and that the relative role of these processes depends sensitively on the energy position of the vacant ionic level relative to that of the valence band; alkali-metal ions have a vacant s level so close to the top of the valence band that the ions are neutralized mainly due to RN. Rare-gas ions such as helium, on the other hand, have the ground state well below the bottom of the valence band so that the ions are thought to be coupled to the band via AN rather than RN. The other ions which we classify as reactive ions, having the ground ionic states between these two extremes, may suffer both processes and their neutralization probability is known to be extremely high compared with alkali-metal ions or rare-gas ions. Among them, hydrogen is of particular interest, as it is the simplest projectile and provides a striking contrast to He^+- or Li^+-ion scattering:[13-15] Although He^+ ions scattered from surface atoms are more likely to remain ionized than those emerging from the bulk and form so-called surface peaks in their energy distributions, H^+ energy distributions usually exhibit no surface peaks but only a broad background extended from zero energy to the maximum ener-

gy corresponding to elastic binary collisions. These remarkable differences have been interpreted on the basis of the model that Auger or resonant coupling between the projectile state and the valence band of the solid must be stronger as the energy level of the projectile approaches the band.[14,16]

The above-mentioned treatment of ion neutralization would be valid for an ion near the surface but, if the distance of the closest approach in a collision is sufficiently small, the interaction may be considered to occur between two atoms colliding in isolation. In the collisional regime, the charge-exchange processes are best described by a molecular-overlap model. In the case of He^+ scattering, indeed, the following two local electronic transition processes are known: (1) If an inner-shell d level of the target atom is located within ± 5 eV of the ground-state He $1s$ level, the He^+ ion is neutralized due to the quasiresonant neutralization (QRN) process.[17,18] (2) If the $1s$ orbital of He^+ is promoted in the molecular state due to antibonding interaction with a target core orbital, energy-level crossing (ELC) with a valence band results in the neutralization of He^+ ions or excitation of valence electrons.[19-21] The promotion depends strongly on the species of the target elements and is suppressed in the case in which the closed d shell of the target is located at an energy position shallower than the vacant -24.6-eV level of He^+. Thus, a molecular-overlap mechanism should exhibit remarkable orbital-symmetry effects. With respect to H^+ scattering, the vacant $1s$ level (-13.6 eV) is located so shallow compared with the He $1s$ level that the interaction with the band rather than the core level is likely to occur. Of particular interest in H^+ scattering, therefore, is the effect of the valence-band structure or symmetry on the electronic transition probability (band effect). So far, band effects have been studied mostly in terms of the bandwidth,[22] but very little has

been discussed in terms of orbital-symmetry effects. The present study, therefore, focuses on this subject.

In the previous papers,[23,24] we have shown that the D$^+$ ions with a primary energy E_0 of about 100 eV are neutralized almost completely at metallic surfaces due to strong resonant coupling of the D $1s$ orbital with the metal s band. It has also been pointed out that, at ionic-compound surfaces, the neutralization process of the D$^+$ ions is simplified because Auger neutralization can be ignored due to a large band gap of the target and the small ionization energy of D$^+$ and, hence, resonant tunneling and energy-level crossing are the main causes for the neutralization of D$^+$. Recently, Tsuneyuki et al.[25] have pointed out that important factors dominating the charge-transfer probability are diffusion of an ionic hole into the band and the formation of a surface molecule which suppresses the diffusion: The hole transferred from the impinging ions diffuses into the band with a lifetime

$$\tau = \hbar/W , \qquad (1)$$

where W is the bandwidth. Hence, D$^+$ is neutralized in case the collision time T is sufficiently long compared with τ. If the interaction matrix element of the D $1s$ orbital with the band V is comparable to W, the surface molecule is formed and hole diffusion is suppressed to some extent. The charge-transfer probability, therefore, is determined from the competition among T, W, and V. In the case of the extended s band, indeed, the neutralization probability of D$^+$ is expected to be high because T is more than 1 order of magnitude larger than τ. On the other hand, when W is smaller, as in the case of the d band of the transition metal, the neutralization probability might be much smaller. Thus, the neutralization probability of D$^+$ is a good probe for the hole diffusion into the band, and it is probable that chemical-state information about compounds can be obtained from the study of the charge-exchange process.

In this paper, we discuss band effects on the charge exchange between low-energy ($10 < E_0 < 300$ eV) D$^+$ and some ionic compounds such as alkali-metal halides, alkaline-earth halides, transition-metal compounds, and rare-earth trifluorides. A remarkable result of the present study is that, while the diffusion of the D $1s$ hole into the p band with a type of rare-gas valence configurations is not rapid compared with the collision time, it is very much enhanced for an anion p band hybridized with cation d states because the intermediate d hole state is coupled strongly to the initial D $1s$ state via resonant charge exchange and to the final anion p state via covalent orbital hybridization.

II. EXPERIMENT

The experimental setup and the procedure have been described elsewhere.[19] The sample chamber, being evacuated down to an ultrahigh-vacuum (UHV) condition (1×10^{-8} Pa), was equipped with facilities for low-energy ($10-10^4$ eV) ion scattering, ultraviolet photoelectron spectroscopy (UPS), and differentially pumped sample evaporation. The D$^+$ions generated in a discharge-type

ion source were collimated and were mass analyzed by a Wien filter. In each ISS measurement, the dose of the D$^+$ beam was kept below 10^{13} atoms/cm^2 in order to minimize surface decomposition due to ion bombardment. The D$^+$ ion beams with an energy spread of about 1 eV were incident upon a surface at a glancing angle of $\alpha = 80°$ and ions reflected with a scattering angle of $\Theta = 160°$ were analyzed by a hemispherical electrostatic energy analyzer operating with a constant energy resolution of 1 eV.

The following ionic compounds with different electronic band structures were carefully selected to investigate band effects on the charge-exchange probability: LiF, MnCl$_2$, CoCl$_2$, SrCl$_2$, ZrO$_2$, CdCl$_2$, LaF$_3$, PrF$_3$, SmF$_3$, and TmF$_3$. A thin film of ZrO$_2$ was grown by exposing a sputter-cleaned polycrystalline zirconium surface to oxygen.[26] The other samples were polycrystalline thin films evaporated in situ from a tantalum boat onto a smooth substrate of graphite at ambient temperature. The sample charging due to ion-beam bombardment of these insulators is estimated to be below a few eV from the cutoff energy of the secondary ions. It is known that evaporated thin films of these compounds are good for studies of the bulk electronic properties.[20,27,28] Since some of these materials (MnCl$_2$, CoCl$_2$, SrCl$_2$, CdCl$_2$) are hygroscopic, they were baked in a vacuum for a long time before they were used as starting materials for evaporation. The pressure in the spectrometer chamber rose from 1×10^{-8} to 5×10^{-6} Pa during evaporation.

III. RESULTS AND DISCUSSION

In previous papers,[23,24] we have shown that the surface peak of D$^+$ ions, which is usually very weak or completely absent in the D$^+$ energy distribution from metal surfaces, appears with high intensity in those from the alkali-metal halide or alkaline-earth halide surfaces. This is mainly because the metal s band, which is most important for the neutralization of D$^+$, is pushed up to an empty conduction band. For these compounds, therefore, the D $1s$ orbital can interact with the p band which has a type of rare-gas valence configuration. The dependence of neutralization and inelastic scattering of D$^+$ on the p-band energy position relative to the D $1s$ level will be discussed in Sec. III A.

Among various ionic compounds, the transition-metal and rare-earth compounds are of particular interest concerning the behavior of the cationic d and f states, respectively. Indeed, transition-metal chlorides such as MnCl$_2$ and CoCl$_2$ occupy a special place in condensed-matter physics owing to the apparent incompatibility of the insulating behavior with the partial occupation of the d shell. The Mott insulator concept resolves this incompatibility;[29] since a large d-d Coulomb interaction exceeds the d-band width, the metal d electrons are localized and exist in states like those in free atoms, while the empty s state and filled anion p state form bands. The effect of cationic $3d$ and $4f$ states on hole diffusion into the band will be discussed in Sec. III B.

As has been mentioned in Sec. I, the energy distribution of D$^+$ is characterized by the extended background,

which tends to increase in intensity at oxygen-adsorbed metal surfaces or ionic-compound surfaces, and exceeds surface peak intensity at higher energies. The background is not due to surface scattering but due to reionization of neutral D^0 scattered from the bulk.[23,24] This is confirmed from the fact that the surface peak of D^+ surviving neutralization, though retaining a very low intensity at the clean Mo(111) surface, disappears completely due to oxygen chemisorption while the background is largely increased instead, and that the background D^+ spectrum is essentially the same as that caused by the ionization of a neutral D^0 beam in the ground state. In the present study, we are concerned only with the surface peak, so that experiments shown below were performed using a D^+ beam with E_0 as small as 300 eV or below.

A. Alkali-metal halides and alkaline-earth halides

It has already been shown in previous papers[23,30] that the surface peaks corresponding to each element of KI, BaF_2, and CsCl are composed of two peaks: one is due to elastic single scattering (peak A) and the other is due to inelastic single scattering (peak B) caused by the excitation of a valence electron to the conduction band. In the case of D^+ scattering from Cl^- at LiCl,[23] it has been shown that the intensity of peak A decreases steeply above the threshold energy of 30 eV where the loss peak B appears simultaneously. These behaviors have been interpreted on the basis of the ELC process that the D 1s orbital, promoted in the molecular state with Cl^- ions, crosses the valence band at an internuclear distance of about 0.8 Å. It should be noted that the threshold energy for ELC of these ionic compounds is usually as small as 100 eV or below.

Shown in Fig. 1 are the energy spectra of D^+ scattered from $SrCl_2$; the measurements were made using a D^+ beam with primary energy E_0 of (a) 200 eV and (b) 100 eV. The energy position corresponding to the elastic binary collision for each element is indicated by an arrow along the abscissa axis. The background intensity due to reionization of D^0 is shown by a dashed line. Similar to the D^+ spectra already reported, the surface peak of each element is composed of two peaks, A and B. The energy difference between peaks A and B, therefore, corresponds approximately to the band-gap energy of $SrCl_2$. By comparing the energy spectrum in Fig. 1(a) with that of He^+ scattering,[19] it is found that the intensity of the Cl peak relative to that of the Sr peak is smaller in He^+ scattering and an additional loss peak appears in the He^+ spectra. The former may be due to an additional contribution of the Auger process, especially to He^+ scattering from Cl^-, and the latter will be discussed later.

Figure 2 shows energy spectra of D^+ scattered from LiF. The spectra are made up of a clear surface peak and a large background due to reionization. In contrast to Fig. 1, the surface peak for the F^- ions is composed only of peak A. One may be inclined to think that the absence of the loss peak B is a peculiarity of the D^+ being scattered from F^- ions, but this notion is quickly discarded because peak B is clearly seen in the spectra from $BaF_2(111)$.[23] The absence of the loss peak B, therefore,

may be correlated with the band structure of LiF. The surface peak appears at an energy position about 2 eV above that of the ideal binary collision shown by the arrow. This shift in the peak position is probably caused by the charging effect, which is often observed in the spectral peak from anions, although no shift is seen in that from cations[23] (see also Figs. 4, 6, and 8). The origin of these curious peak shifts, however, is not clarified. The surface peak for Li^+ is not clearly distinguishable from the background. This is probably due to the small cross section and large neutralization probability in D^+-Li^+ scattering. In this respect, it is notable that the surface peak of H^+ scattered from Li^+ clearly appears even for $E_0 = 100$ eV though its intensity is more than 1 order of magnitude smaller than the F^- peak intensity, suggesting that the neutralization probability depends on the velocity of the ions.
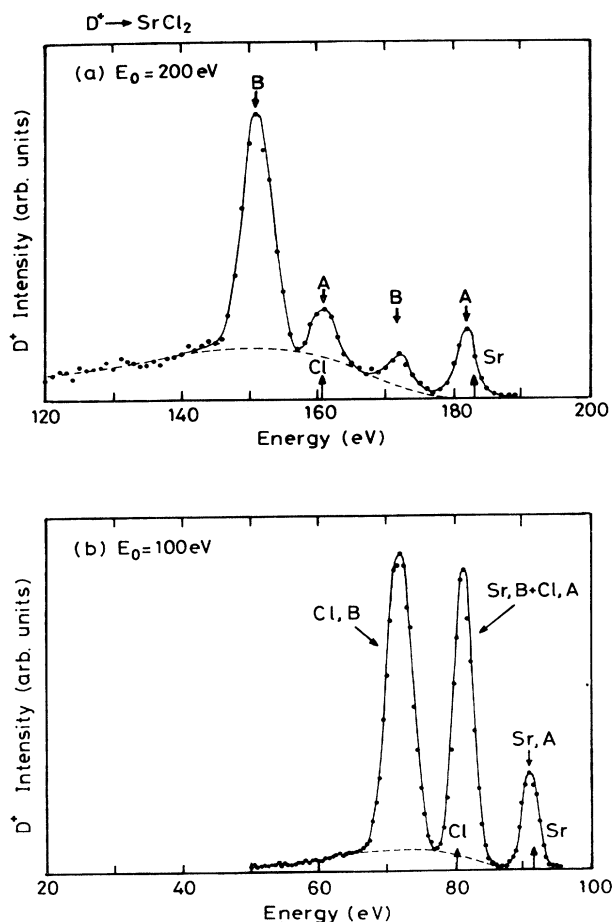

FIG. 1. Energy spectra of D^+ ions scattered from a polycrystalline $SrCl_2$ film. The measurements were made using a D^+ beam of (a) 200 eV and (b) 100 eV at a fixed scattering geometry, $\alpha = 80°$, $\Theta = 160°$. The background due to reionization of neutral D^0 scattered from the bulk is shown by the dashed lines. The energies for elastic binary collision are indicated by arrows on the abscissa. The lines are drawn to guide the eye.

The electronic band structure of the relevant compounds determined by UPS, together with the D $1s$ and He $1s$ levels, is presented in Fig. 3.[27,31,32] The valence band is only composed of the closed p shells (a type of rare-gas valence configuration). The anion p band, except for LiF, is located above the D $1s$ state while the p band of the cations, clearly separated from the anion p band, is located below it. Considering the experimental result that the loss peak B has been observed for all these anions except for the case of F^- in LiF and excitation of the cation p-band electron is not observed in D^+ scattering, we can conclude that the electronic excitation in D^+ scattering is caused by the ELC process in which only the p-band electron with a binding energy smaller than the D $1s$ level can be excited. Of particular interest is LiF since the F $2p$ band overlaps with the D $1s$ orbital in energy without any promotion of the D $1s$ orbital. For LiF, indeed, the intensity of peak A versus the primary energy E_0 exhibits no threshold energy characteristic of ELC in addition to the disappearance of the loss peak B. It is thus found that the ELC process is inhibited if the binding energy of the band is smaller than, or equal to, that of
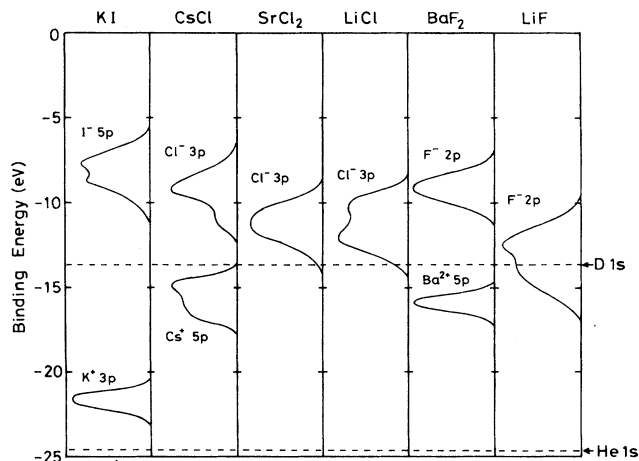
FIG. 3. Valence-band photoemission spectra of the alkali-metal halides and the alkaline-earth halides. The intensities of the spectra are not related.

the D $1s$ level.

One of the most striking discrepancies between D^+ scattering and He^+ scattering is the absence of the second loss peak exhibited by He^+ on anions. It is known in He^+ scattering[19] that the second loss peak relevant to simultaneous two-electronic excitation from the anion p band usually appears in the spectral peak of anions. The absence of this peak in D^+ scattering may be related to the location of the D $1s$ state being close to the anion p band. This is consistent with the fact that, while this peak is not seen in the D^+ spectra from Cl^- (CsCl, $SrCl_2$, LiCl) and F^- (BaF_2, LiF), it is observed in the spectra from I^- in KI for which the I $5p$ band has the smallest binding energy among the compounds shown in Fig. 3.[30]

Since the F $2p$ band of LiF overlaps in energy with the D $1s$ level, one may claim that the contribution of RN must be taken into consideration in addition to ELC discussed above. As mentioned in Sec. I, the probability for RN is determined by the lifetime τ of the hole which diffuses into the p band. With use of a width of the F $2p$ band of 5 eV, a lifetime of the hole of 1×10^{-16} sec is obtained. Since τ is about 1 order of magnitude smaller than the collision time T of D^+ on LiF, it is anticipated that D^+ is neutralized almost completely. In reality, the intensity of the D^+ surface peak for LiF is comparable to that for other compounds shown in Fig. 3. This result strongly suggests that the ELC process is essential in the coupling of the D $1s$ state with the p band having a rare-gas valence configuration and that the contribution of RN is largely suppressed probably due to formation of the surface molecule.[25]
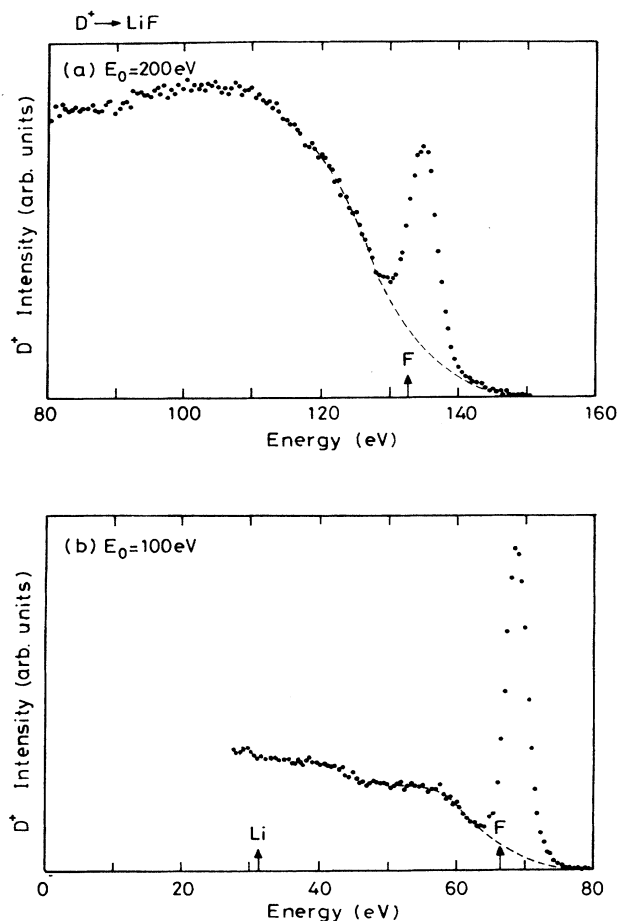

FIG. 2. Energy spectra of D^+ scattered from LiF obtained using a D^+ beam of (a) 200 eV and (b) 100 eV. The background D^+ intensities are shown by dashed curves.

B. Transition-metal compounds and rare-earth trifluorides

The energy spectra of D^+ scattered from LaF_3 and ZrO_2 are shown in Figs. 4 and 5, respectively. Though the background is rather large, the surface peak corre-

sponding to each element is clearly seen. As has been reported in an earlier paper,[23] the oxidation of transition metals like Mo and Ta causes no cationic surface peak due to formation of the metallic oxides in which the metal d electron retains the band feature. In contrast to this, the appearance of the cationic surface peaks in Figs. 4 and 5 corresponds to the fact that the metal atoms, losing all of their d electrons, are in the form of La^{3+} and Zr^{4+} ions, and hence the valence band is characterized by the occupied anion p states similar to alkali-metal halides.

The results for the ionic compounds discussed so far can be interpreted on the basis of the band picture but, for the transition metals on the right-hand side of the Periodic Table, the band picture does not hold for describing the cation d state and the existence of the localized ionic-core state must be taken into consideration. Figure 6 shows energy spectra of $E_0 = 100$ eV D^+ ions scattered from a series of isomorphous chlorides such as (a) $MnCl_2$, (b) $CoCl_2$, and (c) $CdCl_2$, having the cadmium chloride lattice. The most remarkable feature of the spectra is the nearly complete absence of the surface peaks corresponding to Mn^{2+} and Co^{2+} ions, whereas the Cd^{2+} surface peak is clearly seen. This result is also confirmed in the energy range from 10 to 500 eV.

The $3d$ electrons in Mn^{2+} and Co^{2+} are localized enough to retain their atomic nature with the d^5 and d^7 configuration, respectively, while the $4d$ electrons in

Cd^{2+} form a closed d shell. Figure 7 shows UPS valence-band spectra of (a) $MnCl_2$, (b) $CoCl_2$, and (c) $CdCl_2$; the background for each spectrum has been subtracted. Photoemission of valence electrons in strongly correlated systems such as $MnCl_2$ and $CoCl_2$ is known to exhibit many-body effects due to d-d Coulomb interaction and configuration interaction,[29] and the peak assignment rests on an analysis of the energy of the final hole state. According to the local-cluster theory,[33] the hatched peaks for $MnCl_2$ and $CoCl_2$ have been attributed mainly to the $3d^nL$ final state, where L denotes a ligand hole state, and the center of the $3d^{n-1}$ final state, which is not explicitly shown in Figs. 7(a) and 7(b), is located at several eV below it. Thus, the cation d state is extended and overlaps energetically with the Cl $3p$ valence band.

This remarkable D^+ spectral feature of $MnCl_2$ and $CoCl_2$ arises from their localized $3d$ states. In He^+ scattering, it is known that the ionic $1s$ state is coupled to the target d state via QRN. As has already been mentioned, the QRN process does not strictly meet the resonance condition but it nevertheless occurs, provided that the d state is located within ± 5 eV of the ionic $1s$ state. This criterion may be applicable to the D $1s$ state and is met not only for Mn^{2+} ($3d^5$) and Co^{2+} ($3d^7$) but also for Cd^{2+} ($4d^{10}$). If the resonant tunneling involves the iso-
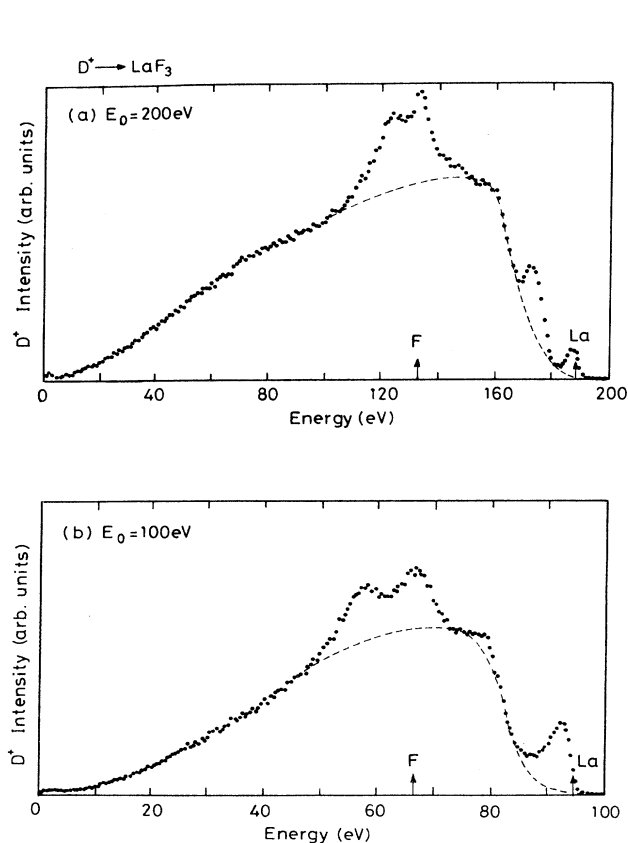

FIG. 4. Energy spectra of D^+ scattered from LaF_3 obtained using a D^+ beam of (a) 200 eV and (b) 100 eV. The background D^+ intensities are shown by dashed curves.
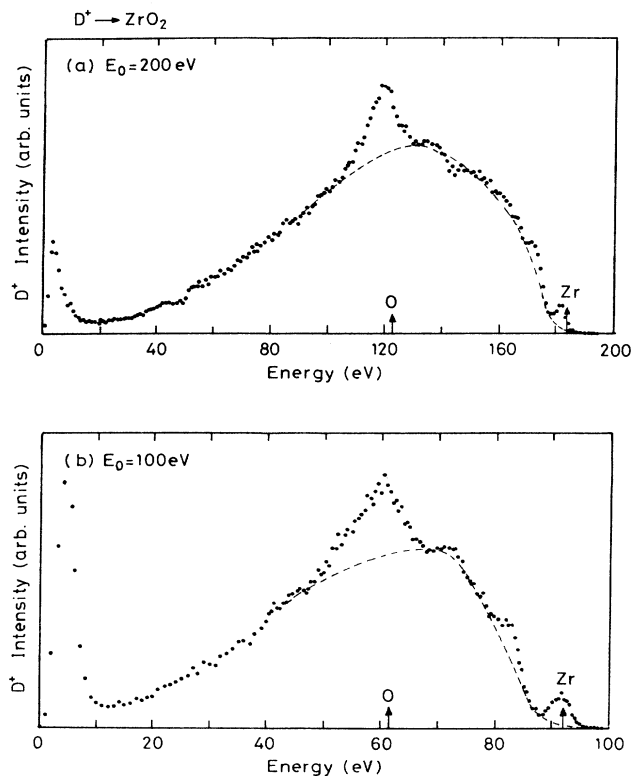
FIG. 5. Energy spectra of D^+ scattered from a thin film of ZrO_2 grown on a polycrystalline Zr surface. The measurements were made using a D^+ beam of (a) 200 eV and (b) 100 eV. The broad background extended from zero energy to the elastic binary-collision energy for Zr is shown by a dashed line.

lated d-core state, a remarkable oscillation appears in the neutralization probability.[17,18] The oscillation results from the quantum-mechanical interference of the molecular orbitals, which occurs only if the electron transition rate is as high as the inverse of the collision time (10^{-15} sec^{-1}). Since the hole once transferred to the band can escape from the target with a lifetime τ ($=\hbar/W$), the interference effects decrease slowing with increasing W. Then the averaged neutralization probability increases from 0.5 at the isolated-narrow-band limit (QRN) to unity at the other, wideband extreme (RN).[25] In terms of the transition-metal chlorides, the localized d state can hybridize with the anion p band and therefore the $3d$ hole state generated by QRN can readily diffuse into the ligand p-band state. If diffusion occurs efficiently within the collision time, D$^+$ remains neutralized with a much higher probability than expected from the isolated-small-band limit. This is the case for MnCl$_2$ and CoCl$_2$. On the other hand, the diffusion of the Cd $4d$ hole state into the band is strongly suppressed because of the isolation of the Cd $4d$ state from the Cl $3p$ band, so that the surface peak for Cd^{2+} is clearly seen in the energy spectrum. Thus, a large transition rate of the hole in the three-body

system, D $1s$–cation $3d$–Cl $3p$, is responsible for the absence of the surface peak. In this context, it should be noted that diffusion of the D $1s$ hole into the anion p band occurs much more efficiently via the intermediate d-hole state than in the direct collision of D$^+$ with anions as discussed in Sec. III A. This clearly indicates that the electron transition rate for (Q)RN is much higher than that for ELC. It is worthwhile noting that the charge-transfer probability cannot be described only by the bandwidth W. Since a rapid diffusion of the hole is evidence for orbital hybridization or covalency of the chemical bonding, the charge-transfer probability may yield information about the chemical state of compounds or adsorbates. The present study implies that the D $1s$–TM (transition metal) d and TM d–anion p bonding has more covalent nature in the orbital hybridization than the coupling of D $1s$ with the anion p band.

The coupling of the D $1s$ state with the valence band of the rare-earth trifluorides is also of interest in comparison with the localized d state of the TM compounds, since the partially filled $4f$ state, located well below the Fermi level, is quite atomiclike and overlaps with the F $2p$ band in energy.[34] Hence, the resonant condition in energy with the D $1s$ state is met satisfactorily for both f and p states. Figure 8 shows energy spectra of $E_0 = 100$ eV D$^+$ scattered from (a) PrF$_3$, (b) SmF$_3$, and (c) TmF$_3$. The spectral features are quite similar to those of LaF$_3$ shown in Fig. 4; clear surface peaks of both cations and F$^-$ ions are found superposed on the large background. It is thus found that the localized $4f^2$, $4f^5$, and $4f^{12}$ states of Pr^{3+},
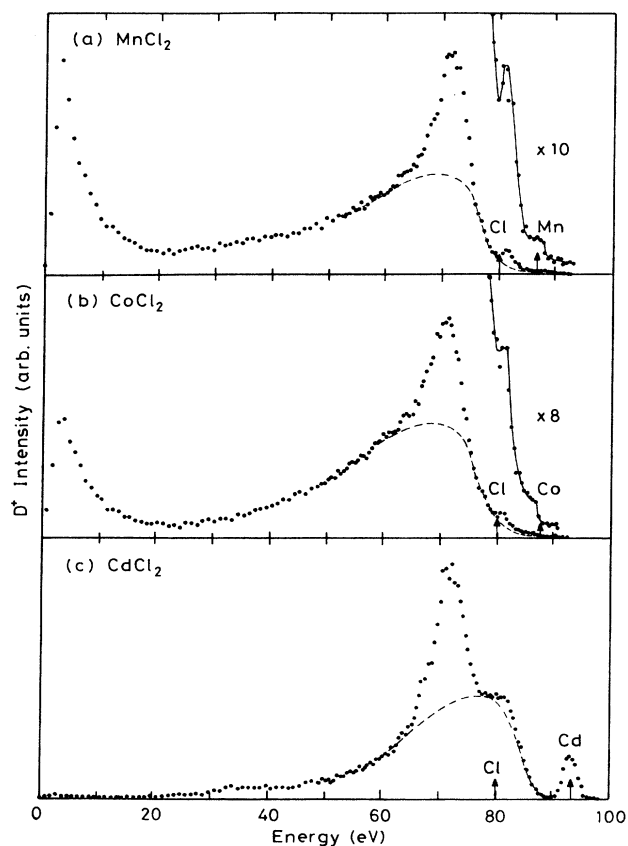

FIG. 6. Energy spectra of D$^+$ scattered from isomorphous chlorides with a cadmium chloride structure: (a) MnCl$_2$, (b) CoCl$_2$, and (c) CdCl$_2$. The measurements were made using a D$^+$ beam of 100 eV. The backgrounds due to reionization of D^0 are shown by dashed lines.
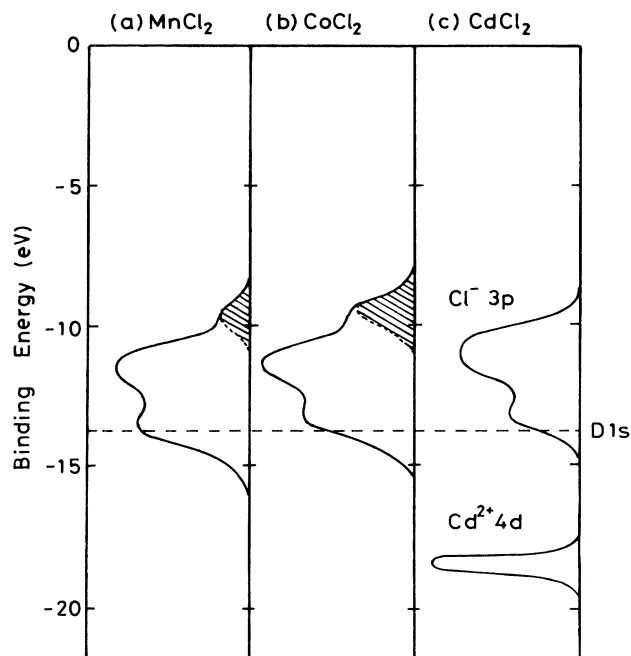

FIG. 7. Valence-band photoemission spectra of (a) MnCl$_2$, (b) CoCl$_2$, and (c) CdCl$_2$; the backgrounds are subtracted. The hatched peaks have been attributed to the $3d^4L$ (MnCl$_2$) and $3d^6L$ (CoCl$_2$) final states, where L denotes the Cl$^-$ hole state.

Sm^{3+}, and Tm^{3+}, respectively, have no influence on the appearance of the cationic surface peak. That is to say, the hole diffusion into the F $2p$ band is not enhanced by the existence of the $4f$ state. This result strongly suggests that the coupling in D $1s$–RE (rare-earth) $4f$ and/or RE $4f$–F $2p$ is not as efficient for the hole diffusion compared with the above-mentioned (D $1s$–TM $3d$–Cl $3p$) hybridization. Indeed, it has been pointed out that x-ray photoemission spectroscopy (XPS) spectral peaks corresponding to the $4f$ state can be interpreted in terms only of the final hole state $4f^{n-1}$ and effects of configuration interaction can be ruled out.[34] Hence, even if the $4f$ hole state is produced due to interaction with D^+, it may survive without diffusion. In addition, the coupling of the D $1s$ hole state with the RE $4f$ state may not be caused by resonant tunneling, which is inferred from the He^+ scattering that the oscillatory

yield curves, which is evidence for QRN, has not been reported in scattering from Hf although the Hf $4f$ state well satisfies the energy resonance condition with the He $1s$ level.[17] Because of the weak coupling among the D $1s$, RE $4f$, and F $2p$ states, the hole tends to remain localized in the D $1s$ state during collision.

The present study clearly indicates that neutralization or inelastic scattering of the low-energy D^+ ions is useful for probing the bonding nature of the solid surfaces. These features arise from the strong coupling of the D $1s$ level with the valence band, which is mainly due to the specific energy position of the D $1s$ level just below the bottom of the valence band. Hence, similar results are also expected to be obtained in H^+ scattering. In terms of other ions such as He^+ and alkali-metal ions, we have reported[32] that effects of chemical bonding appear in inelastic scattering due to the electron-hole pair excitation via the ELC process, while they are not as significant in (Q)RN because the vacant ionic level is located far deeper (He^+) or shallower (Li^+, Na^+, K^+) than the valence band of the compounds discussed here. D^+ scattering with a larger kinetic energy (> 1 keV) than in the present study will probably yield similar chemical-state information about the surface. However, the decrease in the intensity of the surface peak relative to that of the background makes it difficult to discuss chemical effects precisely from the surface peaks alone.

IV. CONCLUSIONS

We have studied band effects on charge exchange in low-energy D^+ scattering from various ionic crystals. The chemical bonding or the orbital hybridization between the D $1s$ state and the various valence-electronic states of the surfaces has been investigated on the basis of the charge-transfer probability. We find the evidence that the probability for the D $1s$ hole diffusion into the surface depends strongly on the symmetry of target electronic states. The coupling of the D $1s$ state with the band having the inert-gas valence configuration, such as alkali-metal halides and alkaline-earth halides, is mainly due to the energy-level-crossing mechanism rather than the resonant charge-exchange mechanism because the diffusion of the D $1s$ hole into the anion p band is suppressed, probably due to the formation of the surface molecule. In addition to these simple ionic crystals, the surface peak has been observed in the D^+ spectra from some transition-metal compounds such as LaF_3 and ZrO_2 for which the cations have no valence d electrons and hence the valence band is characterized by the closed p shell similar to the simple ionic compounds. Of particular interest is the effect of the localized cation d state on the diffusion of the hole. The intermediate d-hole state is responsible for the rapid D $1s$ hole diffusion into the anion p band because of the strong orbital hybridization via the resonant coupling of D $1s$ with the cation d state and covalency in the cation d–anion p bonding. Specifically, the surface peak of D^+ from Mn^{2+} ($MnCl_2$) and Co^{2+} ($CoCl_2$) disappears nearly completely while that from Cd^{2+} ($CdCl_2$) is clearly seen. The atomic $3d^5$ (Mn^{2+}) and $3d^7$ (Co^{2+}) states are located very close to or
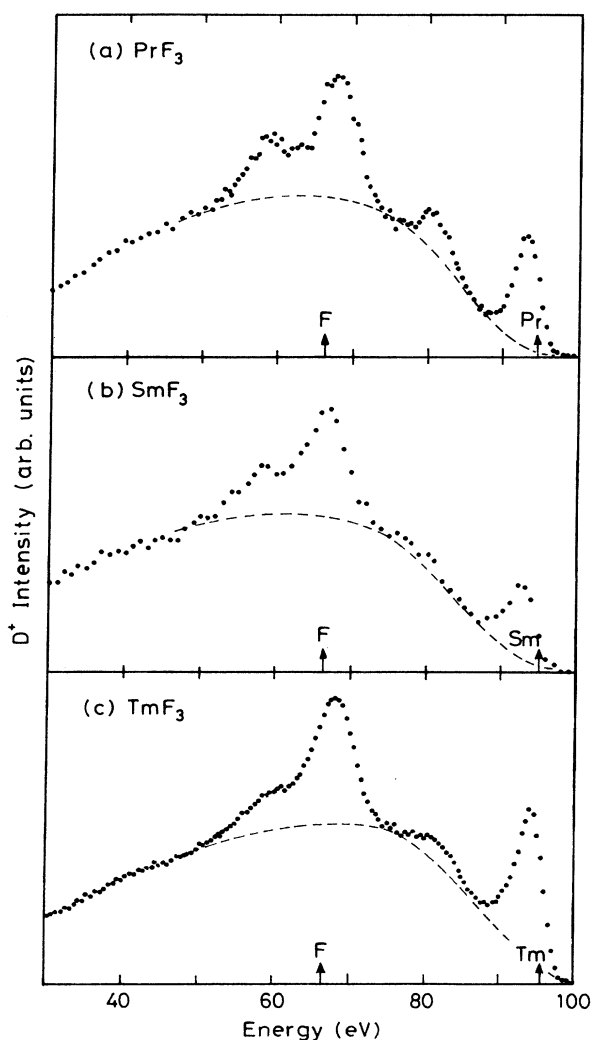

FIG. 8. Energy spectra of D^+ scattered from the isomorphous rare-earth trifluorides; (a) PrF_3, (b) SmF_3, and (c) TmF_3. The measurements were made using a D^+ beam of 100 eV under the same condition as in Fig. 4(b).

completely overlapped with the anion p band, whereas the $4d^{10}$ closed shell of the Cd^{2+} ions are separated so far from the band that covalent orbital hybridization between these two states may be small. Thus, the absence of the surface peaks for Mn^{2+} or Co^{2+} can be ascribed to the resonant charge transfer followed by ligand-to-$3d$ charge-transfer transition. In this respect, the coupling of the D $1s$ level with the valence state of rare-earth trifluorides has been examined. Although energy reso-

nance conditions are satisfied for both the F $2p$ band and rare-earth $4f$ states, the neutralization of D$^+$ on Pr^{3+} (PrF$_3$), Sm^{3+} (SmF$_3$), and Tm^{3+} (TmF$_3$) is not enhanced compared with that on La^{3+} (LaF$_3$), which have no $4f$ state. This is because the resonant coupling of D $1s$ with cation $4f$ and/or the covalency between cation $4f$ and F $2p$ is so small that the D $1s$ hole cannot easily diffuse into the F $2p$ band.

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