Electronic properties of metal induced gap states at insulator/metal interfaces
— dependence on the alkali halide and the possibility of excitonic mechanism of superconductivity

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Motivated from the experimental observation of metal induced gap states (MIGS) at insulator/metal interfaces by Kiguchi et al. [Phys. Rev. Lett. 90, 196803 (2003)], we have theoretically investigated the electronic properties of MIGS at interfaces between various alkali halides and a metal represented by a jellium with the first-principles density functional method. We have found that, on top of the usual evanescent state, MIGS generally have a long tail on halogen sites with a $p_z$-like character, whose penetration depth ($\lambda$) is as large as half the lattice constant of bulk alkali halides. This implies that $\lambda$, while little dependent on the carrier density in the jellium, is dominated by the lattice constant (hence by energy gap) of the alkali halide, where $\lambda_{LiF} < \lambda_{LiCl} < \lambda_{LiI}$. We also propose a possibility of the MIGS working favorably for the exciton-mediated superconductivity.

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I. INTRODUCTION

Heterointerfaces, namely solid-solid interfaces between very dissimilar materials, have been an issue of great interest in condensed matter physics, where various fascinating possibilities may be considered. Especially, the electronic structure of metal/insulator or metal/semiconductor interfaces has a long history of intensive studies dating back to the 1930’s¹,².

One of the most crucial factors which govern the electronic structure of heterointerfaces is the metal-induced gap states (MIGS), whose eigenenergies lie in the band gap of the semiconductor (or insulator). While MIGS spread well into the metal side of the interface, they decay exponentially into the semiconductor. The decay length is an order of a few Å for typical semiconductors, where MIGS have been believed to determine the Schottky barrier height³–⁸.

If we have an insulator/metal interface rather than a semiconductor/metal interface, on the other hand, it has generally been believed that the decay length of the MIGS into the insulator is negligible. This view has been based on quite a plausible model calculation, where the insulator/metal is represented by a simple tight-binding model/jellium⁹. For a typical ionic insulator such as LiCl, the band gap ($\sim O(10)$ eV) is an order of magnitude greater than the transfer energy ($\sim O(1)$ eV) between the cations and anions, and the decay length is estimated to be smaller than 1 Å, which would suggest that MIGS should be irrelevant at insulator/metal interfaces.

Experimentally, it is difficult to detect MIGS at the heterointerface between wide gap insulators and metal, because clean interfaces are difficult to be fabricated. While MIGS have been reported in MgO/Cu(222)¹⁰ or MgO/Ag(001)¹¹, the question of whether the observed gap states are formed by local chemical bonding remained, since MgO(222) is a polar surface so that a strong hybridization between the O 2p band and the Ag 5sp band is expected for MgO/Ag¹³.

Recently, Kiguchi et al.¹² have succeeded in observing MIGS at LiCl/Cu and LiCl/Ag interfaces. They have grown a LiCl film on a metal substrate in a layer-by-layer fashion, and exploiting the near edge x-ray absorption fine structure (NEXAFS) which is an element-selective method, they have observed an extra peak below the bulk edge onset for LiCl film, which was interpreted as an evidence for MIGS. The reason why the detection eluded earlier studies is that, in conventional methods such as ultraviolet photoemission spectroscopy(UPS), inverse photoemission spectroscopy, or electron energy loss spectroscopy(EELS), the signal from the interface is obscured by significant contributions from the substrate. Kiguchi et al. have estimated the decay length of MIGS, which are 2.6 ± 0.3 Å for LiCl/Cu(001) and 2.9 ± 0.7 Å for LiCl/Ag(001), values much greater than those expected in simple models⁹. An ab initio electronic structure calculation for LiCl/metal system has supported the existence of the MIGS that is strongly localized at the interface¹².

The purpose of the present paper is to study the electronic structure of interfaces between various alkali halides and a metal by means of first principles calculation, and to search for novel possibilities specific to metal/insulator interfaces. We shall show that (i) MIGS have a tail on halogen sites with a $p_z$-like character, whose penetration depth ($\lambda$) is as large as half the lattice constant of the bulk alkali halide, which are totally consistent with the experimental result¹², (ii) while $\lambda$ is insensitive to the carrier density in the metal, the pene-
tration depth is dominated by the energy gap of the alkali halide. Specifically, the band gaps are $E_{\text{LiF}} > E_{\text{LiCl}} > E_{\text{LiI}}$, and the the penetration depth has the expected inequality, $\lambda_{\text{LiF}} < \lambda_{\text{LiCl}} < \lambda_{\text{LiI}}$.

We can consider various possibilities for many-body effects unique to heterointerfaces. There is in fact a long history for those, where the notable ones include metal-insulator transition$^{14}$ and superconductivity$^{15,16,18,17}$. In the context of the latter, here we propose that large density of states arising from the MIGS inside the insulator is a good news for the superconductivity due to the exciton mechanism. The history of the exciton mechanism of superconductivity dates back to the proposals by Little$^{15}$, Ginzburg$^{16,18}$, and Bardeen et al$^{17}$. For this mechanism, the coexistence, in real space, of dispersionless excitons and metallic carriers is required$^{17}$. While this is difficult to achieve in general, if the density of states due to MIGS inside the insulator is large enough, we may envisage that the insulator/metal interface such as those discussed here may provide a possible ground for superconductivity. We shall discuss this toward the end of the paper.

II. METHOD

The electronic structure of MIGS is studied with a first-principles calculation based on the density functional theory. We adopt the exchange-correlation functional introduced by Perdew, Burke and Wang$^{19}$ and ultra-soft pseudo-potentials$^{20,21}$ in a separable form. We have first calculated the bulk system and determined the lattices. The obtained values (against experimental ones in parentheses) are 4.09 (4.02) Å for LiF, 5.13 (5.13) Å for LiCl, 5.95 (6.00) Å for LiI and 5.63 (5.63) Å for NaCl.

We have then introduced a slab model, where we put a jellium in the middle of the unit cell sandwiched from top and bottom by an alkali halide layer (Fig.1). Starting from this structure as an initial state, we have performed structure optimization. To confirm that the simplified model with the jellium capture main features in heterostructures with real metals, we have also studied the system where five layers of Cu is considered in place of the jellium. The lattice mismatch between LiCl and Cu happens to be small, so that we can take a small unit cell. The cut-off energy of the plane-wave expansion for the wave functions are 20.25 Ry for LiF, LiCl and LiI/jellium, 25.00 Ry for NaCl/jellium, and 56.25 Ry for LiCl/Cu. The atomic configurations and the corresponding electronic states in the ground states are obtained with the conjugate gradient scheme$^{22}$.

![Fig. 1. Front(a,b) and top(c) views of the atomic configuration considered in the present study. In a(b) one (two) layer(s) of alkali halide sandwich a metal region modeled by a jellium, where solid (open) circles denote cation (anion) atoms while shaded regions the jellium. Unit cells are indicated.](image)

The local density of states is calculated as $\sum_i |\phi_i(x, y, z)|^2$, where $\phi_i$’s are eigenfunctions and the summation is taken over a window $E_F < E_i < E_F + 0.5$eV with $E_F$ being the Fermi energy. We have set the window above $E_F$ to compare with the experiment, where the NEXAFS$^{12}$ detects the unoccupied states.

III. RESULTS

A. LiCl

Let us first discuss the case of LiCl/jellium. Since MIGS have been observed both in LiCl/Cu(commensurate) and LiCl/Ag(incommensurate)$^{12}$, the commensurability in the lattice constants across the heterointerface should not be essential for the formation of MIGS, as we shall confirm below from the results for LiCl/Cu and LiCl/jellium. So we start with the jellium model.

We show in Fig 2(a) the band structure of LiCl/jellium where LiCl layers, each one monolayer thick, sandwiches the jellium that has $r_s = 2.5$. We have also displayed the band structure for an isolated LiCl monolayer. From the comparison we can see that the band structure of LiCl is not severely affected by the presence of the jellium.

It is well-known that GGA or LDA generally underestimate the band gap, while GW approximation$^{23,24}$ improves this. For instance, the band gap for bulk LiCl is 9.2 eV in GW, which is very close to the experimental value of 9.4 eV$^{25}$. However, the band-gap underestimation may be amended via the self-energy correction.
(i.e., without any corrections for LDA wave functions), the shape of the wave functions should be reliable even in LDA, hence the present calculation for LDOS around the $E_F$ is expected to be a good approximation.

In Fig.2(b,c) we have plotted the local density of states (LDOS) integrated along $x$ or $y$-directions. We can see that LDOS has a significant ($\sim$ lattice constant) tail with a $p_z$ character on the halogen site in addition to a usual evanescent-wave like part that exponentially decays away from the interface. In the experiment$^{12}$, while there is no information on Li sites since the element-selective NEXAFS was tuned for Cl in that experiment, an unoccupied state on Cl sites is observed near $E_F$. They have a $p_z$ character, and spread with a decay length of a few Å. These properties are totally consistent with the present results.

![Figure 2](image1.png)

**FIG. 2.** (a) Band structure for the system where LiCl monolayers sandwich the jellium having $r_s = 2.5$ (left panel) and that for an isolated LiCl (i.e., $r_s = \infty$, right panel). (b) Local density of states (LDOS) for $E_F < E < E_F + 0.5eV$ integrated over $y$-direction. The solid (open) circle denotes Li (Cl). (c) LDOS integrated over both $x$ and $y$ directions. The shaded region indicates the insulator region.

If we now replace the jellium with (five layers of) Cu in Fig.4, we can see that the LDOS for the LiCl/Cu has a long tail just as in the result for the jellium model, so that the characteristic feature of MIGS should not be an artifact of the jellium model.

![Figure 4](image2.png)

**FIG. 4.** A plot similar to Fig.2, when the jellium is replaced with five layers of Cu.

To confirm that the penetration depth of the tail of MIGS is as large as a few Å, we have also calculated a larger system, where LiCl double layers sandwich the jellium. From the band structure and the LDOS in Fig.3 we can see that the MIGS do not penetrate into the second layer of LiCl.

![Figure 3](image3.png)

**FIG. 3.** A plot similar to Fig.2, for a system where LiCl double layers sandwich the jellium having $r_s = 2.5$.

Why MIGS have amplitudes only on Li sites can be explained as follows. In general, MIGS can be divided into two groups: one having a conduction-band character and the other having a valence-band character in the insulator side of the interface. Noguera et al.$^9$ have introduced the energy $E_{ZCP}$, above which MIGS have a valence-band character. While the charge neutrality in the insulator side is satisfied when $E_{ZCP}$ is equal to $E_F$, charge transfer from the insulator to the metal occurs if $E_{ZCP} > E_F$. In Fig.5, we plot the difference in the
valence-charge density $\delta \rho$ between the LiCl+jellium and the isolated LiCl. We can see that, while $\delta \rho$ is positive for most of the insulator region ($0 < z < 2$), it is negative around the Cl site. Thus $E_{ZCP}$ should be higher than $E_F$ in this system, and MIGS should have a tail on the anion sites.

Let us move on to the $r_s$ dependence. In Fig.6, we show the result when $r_s$ is increased from 2.5 to 6.0. We can see that, although LDOS at the interface is smaller than that for $r_s = 2.5$, the decay length for $r_s = 6$ is similar to that for $r_s = 2.5$. Thus we may expect that penetration depth does not sensitively depend on the nature of the metal.

**B. Other alkali halides**

Let us move on to the cases of other alkali halides. We have performed calculations for LiF, LiI and NaCl. The results are shown in Fig.7 for LiF, Fig.8 for LiI, and Fig.9 for NaCl. The results are similar to that for LiCl(Fig.2). Namely, MIGS have a long tail on anion sites with a penetration depth $\lambda$ as large as the layer spacing $a_z = a/2$. The lattice constants are $a = 4.09$ Å for LiF, 5.13 Å (LiCl), 5.95 Å (LiI) and 5.63 Å (NaCl), and $\lambda$ for LiI is indeed the largest (1.5 times as large as that for LiF). Note that anions with higher electron affinity have smaller ionic radii in general, so that alkali halides with larger band gap have smaller lattice constants.
One of the most fascinating possibilities which should be explored for heterointerfaces is, we believe, the exciton-mediated superconductivity. The exciton mechanism has been originally proposed by Little\textsuperscript{15} for metallic, quasi-one dimensional spines of conducting electrons to which dielectric organic molecules are conceived to be attached chemically. Subsequently, two-dimensional version of this mechanism has been proposed\textsuperscript{16–18}, where a metallic film covered by a dielectric coating was considered. To realize the exciton mechanism in general, carriers have to coexist and strongly interact with the excitons. Thus the penetration length must be sufficiently large, which is why it has been believed that the band gap of the coating material should not be too large. On the other hand, Inkson and Anderson\textsuperscript{26} have pointed out that, if we adopt the model dielectric function for typical semiconductors, exciton-electron coupling becomes small, partially because the exciton has a large energy dispersion so that the phase space over which the mechanism works for the formation of paring is restricted. In fact, in Ref.\textsuperscript{17} the energy dispersion of the exciton is ignored. In other words, they have considered a Frenkel exciton, which is usually unrealistic for (narrow gap) semiconductors.

Now, the present result for MIGS at metal/insulator interfaces can reconcile the very dilemma. Namely, while a conventional wisdom tells that the penetration depth should be extremely small for metal/wide-gap insulator interfaces, the present result suggests that the depth is of the order of the lattice constant for the MIGS, so that a substantial portion of the carriers can interact with the exciton in the insulator side. Thus it becomes an intriguing problem to estimate the electron-exciton coupling for the alkali halide/metal system, so we do this following the argument of ref.\textsuperscript{17}.

According to ref.\textsuperscript{17}, the exciton-electron coupling $\lambda_{ex}$ is estimated as $s\gamma^2(D/L)\mu(\omega_p/\omega)^2$, where $s$ is the screening factor for the Coulomb interaction, $\gamma$ the ratio between the LDOS at the interface and that for the bulk, $D$ the average depth of penetration, $L$ the thickness of the metal film, $\mu$ the screened Coulomb interaction averaged over the Fermi surface multiplied by the density of states at $E_F$, $\omega_p$ the electronic plasma frequency, and $\omega$ the band gap of the insulator. If we assume that the dielectric function can be approximated as

$$\varepsilon(\omega) = 1 - \left(\frac{\varepsilon_{\text{optical}} - 1}{\omega^2 - \omega_0^2}\right),$$

where $\omega_0 \sim \omega$ is the typical exciton energy, and $\varepsilon_{\text{optical}}$ the optical dielectric constant, then $\lambda_{ex}$ becomes $s\gamma^2(D/L)\mu(\varepsilon_{\text{optical}} - 1)$.

Let us first look into the factor $\gamma D/L$. This factor is, in the simplified model due to Bardeen, the fraction of the time over which the metal electrons spend in the insulator. In the more realistic model we have at hand, we can more precisely integrate the LDOS in the insulator region ($\equiv \rho_i$, shaded region in Fig.2(c) etc) since MIGS do not possess a monotonic (exponential) LDOS, and we can then divide the quantity by that for the metal region ($\equiv \rho_m$) to obtain the factor corresponding to $\gamma D/L$. Namely, the factor should read $b \equiv 2\rho_i/\rho_m$, in place of $\gamma D/L$, where $a_z = a/2$ (see Fig.1). The present model is a sandwich structure where the metallic layer is covered by the dielectric coatings from both sides, so that the factor 2 appears in r.h.s. Here we set that the thickness of metallic layer to be 10 Å. The resulting values are $b = 0.08$ (for LiF), 0.18(LiCl), 0.16(LiI), and 0.12(NaCl).

On the other hand, $(\varepsilon_{\text{optical}} - 1) = 0.92, 1.68, 2.4$ and 1.33 for LiF, LiCl, LiI and NaCl, respectively\textsuperscript{27}. Therefore, if we adopt the same values for $s(= 1/2)$, $\mu(= 1/3)$, $\gamma(= 1/2)$ as in Ref.\textsuperscript{17}, $\lambda_{ex}$ can become as large as 0.06 for LiI, while we have $\lambda_{ex} = 0.01$(LiF), 0.05(LiCl), and 0.63(NaCl).

If we adopt weak-coupling conventional superconductors, e.g. Al, as the metal, the superconducting transition temperature can be roughly estimated\textsuperscript{18,28} as

$$T_c = \theta \exp\left(-\frac{1}{\lambda_{ph} + \lambda_{ex} - \mu^*}\right),$$

where $\lambda_{ph}$ is the electron-phonon coupling, $\lambda_{ex}$ the electron-exciton coupling, and $\mu^*$ the renormalized $\mu$. So $\theta$ is roughly expressed as

$$\log \theta \propto \int \frac{\rho_{ph}(\omega)(\rho_{ex}(\omega) + \rho_{ph}(\omega))}{\omega} d\omega,$$

where $\rho_{ph}$ ($\rho_{ex}$) is the density of phonon (exciton) states. In general, $\rho_{ph}$ has a peak in a low energy region, so that, when phonons and excitons coexist, the contribution of the phonon part to $\theta$ should be dominant than...
that of the exciton part. Thus $\theta$ basically scales with that of phonon, but the exciton contribution on top of that can enhance the $T_c$ significantly. For example, when $\lambda_{ph} \simeq 0.4$, $\mu^* \simeq 0.05$, and $\lambda_{ex} \simeq 0.1$, $T_c$ becomes 1.6 times greater than that in the bulk. Thus we conclude that heterointerface between metal and LiI or LiCl can be a promising ground for detecting the existence of exciton-enhanced superconductivity.

In addition, the proximity of different systems enables us to expect entirely different mechanism. Namely, two of the present authors\cite{29} have earlier proposed that a class of repulsively interacting systems that consist of a carrier band and an insulating band can become superconducting, where the system can effectively mapped to an attractive Hubbard model. The point is, while the conventional boson-exchange pairing arises due to a retarded attraction, superconductivity in the carrier-insulator model occurs due to a nonretarded attraction. In their model, the metallic band is assumed to interact only with the anion sites (or to interact only with the cation sites). At the interface between an alkali halide and a metal, MIGS have their amplitudes on anion sites, so that the MIGS should interact primarily with anion sites, which just corresponds to the situation considered in Ref.\cite{29}. The detailed study on the combined effect of the nonretarded attraction (which decreases $\mu^*$) and the exciton effect (which increases $\lambda$) is an interesting future problem.

\section*{V. SUMMARY}

We have studied the electronic properties of metal-induced gap states (MIGS) at interfaces between various alkali halides and a metal. We have performed first-principles density functional calculation to show that (i) in addition to a usual evanescent-wave component, MIGS have a tail on halogen sites with $p_z$-like character, whose penetration depth is as large as the lattice constant of the alkali halide, (ii) while $\lambda$ does not significantly depend on the carrier density of jellium, it depends on the energy gap of alkali halides, with $\lambda_{LiF} < \lambda_{LiCl} < \lambda_{LiI}$. We have estimated the electron-exciton coupling, and have found that we may envisage that insulator/metal interfaces such as those discussed in the present study may provide a possible ground for exciton-mediated superconductivity.

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