



ELECTRONIC STRUCTURE AND ELECTRON-PHONON INTERACTION IN TRANSITION METAL OXIDES WITH d^0 CONFIGURATION AND LIGHTLY DOPED COMPOUNDS

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Abstract—While photoemission spectroscopy has been used as a powerful technique to study the electronic structure of solids, it also reflects the dynamical as well as the static properties of the lattice through electron-phonon interaction. In this paper, we present the results of photoemission studies on insulating and lightly carrier-doped oxides and discuss their relevance to the lattice properties of the solids. First, the electronic structure of perovskite-type Ti oxides as well as that of V oxides with empty metal $3d$ bands is deduced and discussed in relation to recent microscopic theories of ferroelectricity. Next, we point out that some spectral features of these oxides, when lightly doped with electrons, indicate a sign of strong coupling between the doped electrons and lattice distortion and hence the polaronic nature of the charged carriers.

Keywords: A. oxides, C. photoelectron spectroscopy, D. electronic structure, D. ferroelectricity, D. phonons.

INTRODUCTION

The electronic properties of solids are determined not only by the motion of electrons themselves but also by the motion of the lattice, which is coupled with the motion of the electrons through the electron-phonon interaction. Photoemission spectroscopy has been used as a powerful tool to investigate the electronic properties of solids, but it also has a capability to yield information about the dynamical properties of the lattice if the electron-phonon interaction is strong enough to modify the photoemission spectra, compared to those predicted for the rigid lattice. In spite of this, the possibility of studying the dynamical properties or the instability of the lattice and the nature of electron-phonon interaction in solids has not been seriously pursued using photoemission spectroscopy. So far, thermal broadening [1], lattice relaxation [2] and simultaneous excitations of bosons (including phonons) [3] in core-level spectroscopy have been discussed in the literature.

In this article, we present results of photoemission studies on some transition metal oxides and attempt to explain unusual aspects of the experimental results in terms of electron-phonon coupling. First, the electronic structure of Ti and V oxides with empty Ti and V $3d$ bands, namely, with formally d^0 configurations, is deduced from the analysis of core-level photoemission spectra and discussed in terms of its relevance to

recent microscopic theories of ferroelectric lattice instabilities [4, 5]. Second, we present spectroscopic evidence for strong electron-phonon coupling in these oxides when they are doped with a small number of electrons. In order to reconcile the large energy scale (1–2 eV) seen in the photoemission spectra with the small energy scale (<0.1 eV) of the transport properties, we propose a model in which the charged carrier interacts with the ionic lattice through both short-range and long-range interactions simultaneously.

ELECTRONIC STRUCTURE OF TRANSITION METAL OXIDES WITH EMPTY d BANDS

The electronic structure of perovskite-type transition metal oxides with empty conduction d bands is of great interest for the studies of ferroelectricity since many ferroelectric oxides belong to this class of compounds: e.g. BaTiO_3 , PbTiO_3 (Ti^{4+}), PbZrO_3 (Zr^{4+}), LiNbO_3 (Nb^{5+}) and LiTaO_3 (Ta^{5+}). Also, SrTiO_3 exhibits complicated lattice instabilities associated with the rotation of the TiO_6 octahedra incipient of ferroelectricity [6]. The importance of the empty d bands in the lattice instabilities has been emphasized in the context of electron-lattice coupling in cubic ReO_3 and distorted WO_3 [7] and in BaTiO_3 and SrTiO_3 [8].

In recent years, the electronic structure of 3d transition metal oxides has been studied using core-level photoemission spectroscopy, and its systematic changes as a function of the atomic number and the formal valence of the transition metal ion has been demonstrated [9, 10]. In analyzing the photoemission spectra, a MO_6 cluster model (M = transition-metal ion) has been employed, where the effects of the on-site d - d interaction and the metal d -oxygen p orbital hybridization have been exactly treated within the model cluster. Three parameters, namely, the p -to- d charge-transfer energy Δ , the d - d on-site Coulomb energy U and the p - d transfer integral ($pd\sigma$) are treated as adjustable parameters which are varied so as to reproduce satellite structures in the measured spectra. Here, Δ is an energy required to transfer an electron from the p orbitals to the d orbitals in the hypothetical ionic ground state, i.e. $\Delta = E(d^{n+1}\underline{L}) - E(d^n)$, where \underline{L} denotes a hole in the p orbitals. According to the analyses, Δ decreases both with atomic number Z and valence v . U slightly increases with Z and v : Thus we crudely obtain $\Delta \sim 26 - 0.6Z - 2.5v$ and $U \sim -2.5 + 0.3Z + 0.5v$ [9].

The above results have been largely based on studies of the oxides of heavy transition metals, Mn to Cu, because the photoemission spectra of these oxides exhibit pronounced satellite structures due to the p -to- d charge-transfer mechanism [11] which facilitate analysis using the cluster model. In light transition metal oxides, on the other hand, the satellite features are less pronounced, making such analyses less precise. Furthermore, another mechanism involving the excitation of excitons at the anion site has been proposed as the origin of the satellites in light transition metal compounds [12]. Recently, Okada and Kotani [13] have analyzed the Ti 2*p* core-level photoemission spectrum of TiO_2 using the cluster model and attributed the satellite structure to the same charge transfer mechanism as that in the heavy transition metal oxides.

We have analyzed the Ti 2*p* core-level photoemission spectrum of $SrTiO_3$ using the cluster model and obtained $\Delta = 4 \pm 2$ eV, $U = 4.5 \pm 0.5$ eV and $(pd\sigma) = 2.6 \pm 0.1$ eV [14]. These values are close to those obtained for TiO_2 [$\Delta \sim 3$ eV, $U = 4$ eV] by Okada and Kotani [13], confirming the conjecture that the parameter values are largely determined by the atomic number and valence of the transition metal ion and not much influenced by the crystal structure. It should be noted that $\Delta \sim U$ in the Ti^{4+} oxides, namely, that the system is intermediate between the Mott-Hubbard ($\Delta < U$) and charge-transfer ($\Delta > U$) regimes of the Zaanen-Sawatzky-Allen diagram although the Ti and V oxides were originally regarded as typical Mott-Hubbard systems [15]. For another d^0

system V_2O_5 , we obtain $\Delta = 0.5 \pm 2$ eV, $U = 5.5 \pm 0.5$ eV and $(pd\sigma) = 3.0 \pm 0.1$ eV, indicating that V_2O_5 (V^{5+}) is in the charge-transfer regime [14]. This is in accordance with the claim by Torrance *et al.* [16] based on their Madelung potential calculations that VO_2 (V^{4+}) is already in the charge-transfer regime rather than in the Mott-Hubbard regime. In Fig. 1, we have plotted the parameter values thus deduced for various transition metal oxides [9, 13, 14, 17-19]. The figure shows expected chemical trends, giving further support to the charge-transfer mechanism in the Ti and V oxides.

In the present cluster model calculations, the ground-state wavefunction is given as a linear combination of the ionic d^0 and charge-transfer $d^1\underline{L}$, $d^2\underline{L}$, ..., configurations. The net d -occupation n_d is calculated using the coefficients of these configurations: $n_d = 1.1 \pm 0.2$ for $SrTiO_3$ and

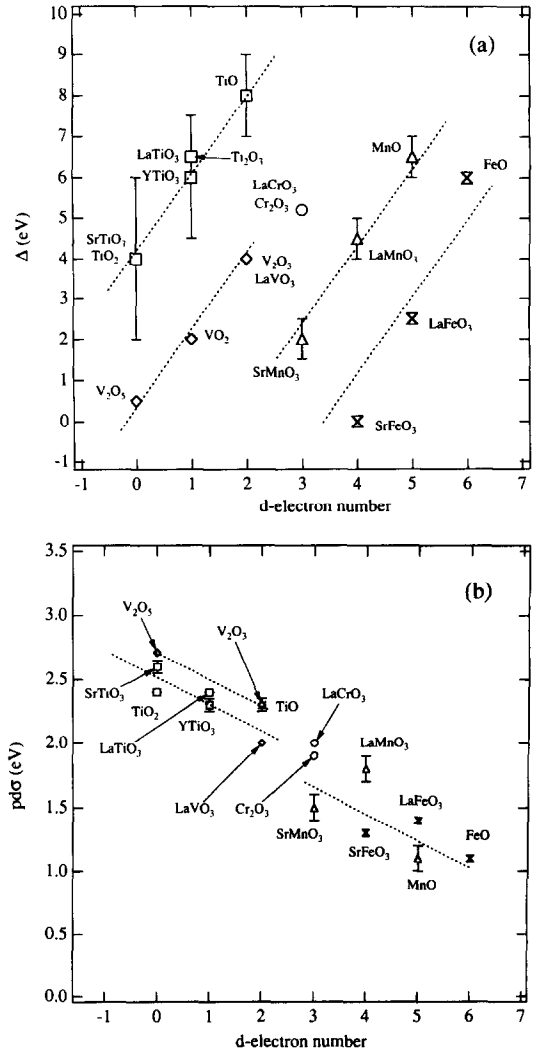


Fig. 1. Systematic changes of the charge-transfer energy Δ and the p - d transfer integral ($pd\sigma$) in 3d transition metal oxides. Ti_2O_3 , VO_2 : [19]; $SrTiO_3$, $LaVO_3$, TiO , V_2O_5 , V_2O_3 , TiO_2 : [14]; Cr_2O_3 : [17]; $LaCrO_3$, $LaTiO_3$: [18], others: [9].

$n_d = 1.5 \pm 0.2$ for V_2O_5 , indicating very strong covalency, namely, a considerable amount of p -to- d charge transfer in the ground state of these oxides. The n_d value for $SrTiO_3$ is in excellent agreement with that given by the band-structure calculation for $BaTiO_3$ [5]. The latter calculation has indicated that the strong covalency between the Ti $3d$ and oxygen $2p$ orbitals is a driving force for the ferroelectric lattice instability of $BaTiO_3$. The strong covalency in $SrTiO_3$ in spite of the sizable magnitude of the Δ value arises from the large ($pd\sigma$) value and the large number of the empty d levels ($=10$) for the formal d^0 configurations. This is contrasted with heavy transition metal oxides, particularly with cuprates, where the strong covalency arises from the proximity of the p and d levels, i.e. from the smallness of Δ .

Recently, Egami *et al.* [4] have proposed that the combination of the p - d hybridization, whose strength depends on the oxygen-metal distance, and electron correlation at the oxygen site enhances the ferroelectric instability of the perovskite oxides. To demonstrate this, a one-dimensional model has been studied using an exact diagonalization technique and it has been shown that the lattice instability is enhanced when Δ is comparable or smaller than the p - d transfer integral. Considering the large error bars for Δ in the light transition metal oxides (see Fig. 1), it can be said that the electronic structure of the perovskite-type Ti oxides is favorable for the ferroelectric instabilities to occur as suggested by Egami *et al.*

SPECTROSCOPIC EVIDENCE FOR ELECTRON-PHONON COUPLING IN LIGHTLY DOPED OXIDES

The photoemission spectra of transition-metal oxides with d^0 configurations (including Ti^{4+} and V^{5+} oxides) are generally well explained by the electronic density of states (DOS) given by standard band-structure calculations [20]. This is because electron-electron correlation does not play a significant role in the filled O $2p$ valence band and in the empty $3d$ conduction band, unlike in Mott insulators, where electron correlation in the partially filled $3d$ band plays an important role [21].

When a small number of electrons are chemically doped into the d^0 oxides, e.g. by La-substitution for Sr atoms in $SrTiO_3$ or by oxygen deficiency, the doped electrons enter the bottom of the empty $3d$ band. In the limit of low doping concentration, there will be no electron correlation between the doped electrons since the probability of electron-electron scattering is vanishingly small. If the doping level is low enough and the system is semiconducting, the doped electrons will be trapped by impurity centers such as the substitutional La atoms or oxygen vacancies. Then, one would

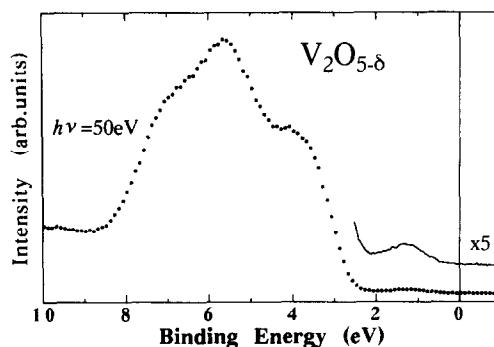


Fig. 2. Photoemission spectra of $V_2O_{5-\delta}$ ($\delta \sim 0.05$) [22].

expect that the photoemission spectra would show a peak whose position measured from the Fermi level (E_F) is the activation energy of the trapped electrons. If the system becomes metallic, the bottom of the $3d$ conduction band is occupied by a small number of electrons and hence the photoemission spectra would show a narrow feature at E_F .

The photoemission spectra of semiconducting $Na_xV_2O_5$ and $V_2O_{5-\delta}$ [22], where the doped electrons occupy the otherwise empty V $3d$ conduction band, show a peak at $E_B \sim 1.2$ eV below E_F as shown in Fig. 2. The peak position is much deeper than that expected from the thermal activation energy (~ 0.2 eV in $V_2O_{5-\delta}$ [23] and ~ 0.03 eV in $Na_{0.33}V_2O_5$ [24]) deduced from transport measurements and is even larger than the energy of the optical absorption peak (~ 0.9 eV in $V_2O_{5-\delta}$) [23]. Figure 3 shows the photoemission spectra of $La_xSr_{1-x}TiO_3$ [25]. Upon

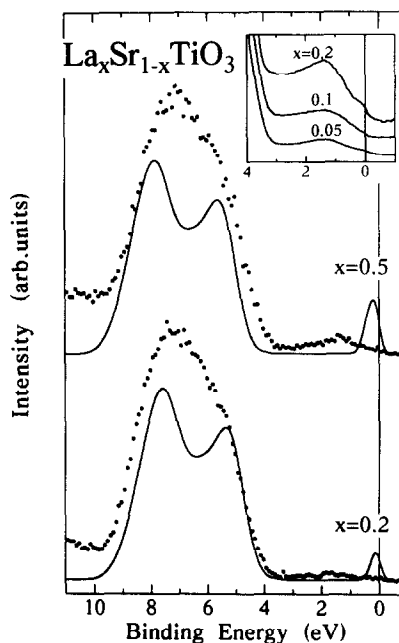


Fig. 3. Photoemission spectra of $La_xSr_{1-x}TiO_3$ (dots) [25] compared with the band-structure calculation (solid curve) [26]. Inset shows spectra near E_F .

La-substitution, new spectral weight appears within the band gap of SrTiO₃, which is formed between the O 2*p* and Ti 3*d* bands. The intensity of the ‘in-gap’ spectral weight increases with La concentration. (The system becomes metallic for *x* as small as 0.05.) The in-gap spectral weight again shows a peak as deep as $E_B \sim 1.5$ eV below E_F , where the activation energy is of the order of ~ 0.01 eV [26], in obvious disagreement with the band DOS [27] as shown by solid curves in Fig. 3.

The discrepancy between the thermal activation energy E_a and the optical transition energy E_{opt} is generally attributed to a polaronic effect: According to small polaron theory based on Holstein’s molecular polaron model, where the electron is coupled to a local lattice distortion through short-range interaction, $E_{\text{opt}} \sim 4E_a$ [28]. If we consider the photoemission process within the same model, the energy E_B of the photoemission peak relative to E_F is only twice as large as the activation energy: $E_B \sim 2E_a$. This is in striking disagreement with the above observation that the peak of the doping-induced spectral weight appears as deep as 1–2 eV whereas the activation energy is of order 0.1 eV or less. According to Frölich’s large polaron model, where the electrons interact with the dielectric polarization of the ionic lattice through the long-range Coulomb interaction, the energy of the photoemission peak is twice as large as the polaron binding energy. Still the observed photoemission peak is too deep to be reconciled with the activation energy.

In order to explain the large discrepancy between the photoemission peak energy and the thermal activation energy, we consider the combined effect of the Holstein-type short-range interaction and the Frölich-type long-range interaction. The latter interaction is particularly important for the photoemission process because a positive unit charge is left in the solid in the photoemission final state: when a photoelectron is emitted, the positive electric charge of the photo-hole interacts with the ionic lattice through the long-range Coulomb interaction. For a polaron of radius r_P , we assume that within the sphere of radius r_P the lattice undergoes a uniform local distortion as represented by the normal coordinate q of the local distortion. Thus the total energy of the coupled electron–phonon system is given by

$$E_1(q, r_P) = E_c + (2\pi/3)nr_P^3 kq^2 - Aq + (\pi^2/2)(\hbar^2/m_b r_P^2) - (e^2/2r_P)(1/\epsilon_\infty - 1/\epsilon_0), \quad (1)$$

where E_c is the energy of an electron at the bottom of the conduction band of the rigid lattice, n is the density

of ‘molecules’, k is the force constant for the local distortion, $-Aq$ is the electron–phonon coupling energy, ϵ_0 and ϵ_∞ are the static and optical dielectric constants and m_b is the conduction band mass. The second term on the right-hand-side of eqn (1) is the elastic energy of the uniform local distortion within the sphere of radius r_P . The last term in eqn (1) represents the interaction between the electric charge of the doped electron and the dielectric polarization of the ionic lattice and the penultimate term gives the kinetic energy of the doped electron within the sphere. We minimize eqn (1) with respect to q to obtain

$$E_1(r_P) = E_c - (3/8\pi)(A^2/nkr_P^3) + (\pi^2/2)(\hbar^2/m_b r_P^2) - (e^2/2r_P)(1/\epsilon_\infty - 1/\epsilon_0). \quad (2)$$

Because the photoemission process occurs suddenly, the local distortion and the dielectric polarization of the ionic lattice do not have time to relax. Thus the photoemission final state has the energy

$$E_0(r_P) = (3/8\pi)(A^2/nkr_P^3) + (e^2/2r_P)(1/\epsilon_\infty - 1/\epsilon_0). \quad (3)$$

In Fig. 4(a), we plot eqns (2) and (3) as functions of $1/r_P$. One can see that the energy of the photoemission peak $E_B [\equiv E_0(r_P)]$ can be much larger than the polaron binding energy $E_P [\equiv E_c - E_1(r_P)]$ and hence than the activation energy E_a . Indeed, if we use typical values for the parameters ($k = 21$ eV/Å² corresponding to the optical phonon frequency of ~ 600 cm^{−1}, $m_b = 7$, $1/\epsilon_\infty - 1/\epsilon_0 = 0.4$, $A = 1.2$ eV/Å), we obtain $E_B \simeq 1.2$ eV, $E_P \simeq 0.4$ eV and $E_a \simeq 0.03$ eV, in reasonable agreement with experiment. The resulting polaron radius is rather small: $r_P \simeq 2.7$ Å. Here, E_a has been calculated using eqn (2) for a simple model, in which the activation barrier is given by the energy of a transient polaron whose radius is expanded so as to accommodate an additional ‘molecule’.

Here, we note that for the short-range electron–phonon interaction, the polaron binding energy becomes largest when the polaron is localized on one atom, whereas for the long-range electron–phonon interaction the polaron binding energy becomes largest for an intermediate polaron size. Therefore, competition between the short-range and long-range interactions makes the polaronic state unstable, making the polaron binding energy and hence the activation energy small. Such a mechanism would tend to delocalize polarons and enhance their mobility, facilitating interesting transport phenomena such as insulator-to-metal transitions and superconductivity. The relationship between E_P , E_B and E_a is schematically displayed in Fig. 4(b). The

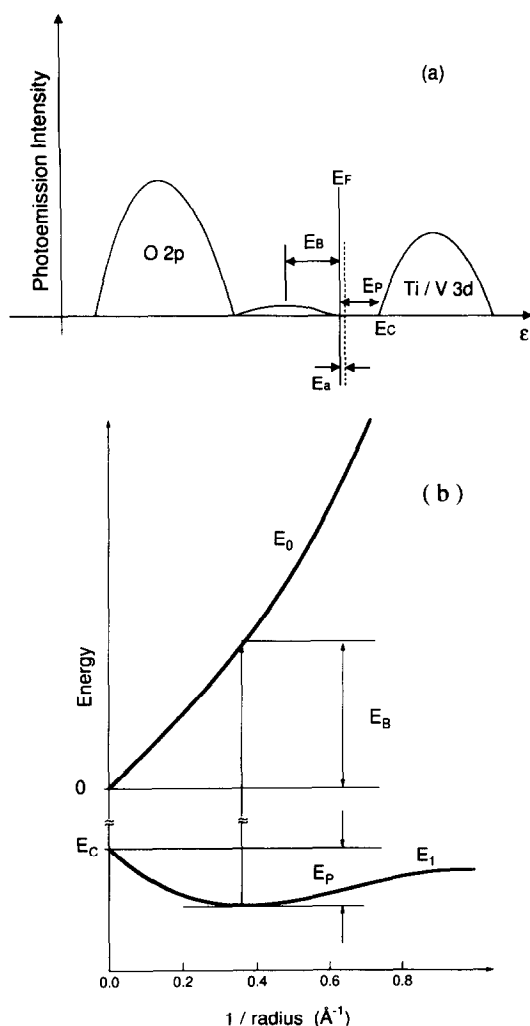


Fig. 4. (a) Energies of the coupled electron-lattice system in the ground state and the photoemission final state as functions of $1/r_p$. (b) Schematic electronic structure of a transition metal oxide with d^0 configuration doped with a small number of electrons. For notation, see text.

experimentally observed large E_B/E_A ratio is an indication of the polaronic nature of the charged carriers.

It is interesting to note that in $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$, the binding energy of the Ti 3d peak does not change with doping up to $x = 1$ [25], where the system becomes a Mott insulator [29]. The V 3d peak position in a Mott insulator LaVO_3 has been discussed by Egdel *et al.* [30], according to which the peak energy is given by $(e^2/2R)(1/\epsilon_\infty - 1/\epsilon_0)$, where R is the radial extent of the localized V 3d electron (hybridized with surrounding O 2p orbitals). This energy will be close to the peak position E_B for the polaron of the combined Frölich-Holstein type proposed above (eqn 3), because the polaron is small ($r_p \sim R$) and the elastic energy [the first term in eqn (3)] is smaller than the dielectric polarization energy [the second term in eqn (3)]. The

deep peak positions in the Mott insulators and their doped compounds would thus indicate the importance of interaction between the photo-hole and the dielectric polarization of the medium. This point has to be clarified in future studies.

CONCLUSION

We have shown that detailed analyses of photoemission spectra yield new information on the nature of electron-phonon coupling in ionic insulators and their carrier-doped compounds. Analyses of core-level photoemission spectra reveal very strong covalency between the metal 3d and oxygen p orbitals for the Ti and V oxides with formally d^0 configuration. The photoemission spectra of the lightly electron-doped compounds suggest the polaronic nature of the doped carriers. Reinterpretation of the photoemission spectra of other doped transition-metal oxides will give new insight into the nature of charged carriers in these compounds.

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