

Correlation between the Madelung field and the reactivity of the MgO low-coordinated surface sites

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We study correlations between Madelung constants, charges of surface ions, and chemical activity of low-coordinated sites of the MgO crystal surface with respect to dissociative adsorption of hydrogen. The *ab initio* Embedded Cluster model [Puchin *et al.*, Phys. Rev. B **47**, 6226 (1993)] employed in this study allowed us to reproduce correctly both short range and long range (Madelung) parts of the interaction between ions in a quantum cluster and the rest of the crystal. Our results show that sites having the same coordination numbers may have different properties, depending on values of Madelung constants. Lower Madelung constants correspond to lower ionicity, higher energy of H₂ adsorption, stronger O–H and Mg–H bonds, and larger spatial separation of two adsorbed hydrogen atoms. © 1995 American Institute of Physics.

I. INTRODUCTION

Apart from being a model system for solid state and surface studies due to its simple crystalline structure and purely ionic bonding, magnesium oxide crystals also exhibit catalytic activity for hydrogen isotope exchange,^{1,2} water–gas shift,³ oxidative coupling of methane,^{4–6} and other reactions. It was established more than two decades ago that chemical activity of the surface of undoped MgO is determined by a small number of defect sites (steps, kinks, corners, etc.) with surface ions (especially oxygen) having low coordination numbers.^{7,8} In particular, dissociative adsorption of hydrogen molecules on the pairs of adjacent low-coordinated O^{2–} and Mg²⁺ ions can take place via heterolytic mechanism,^{9–13} resulting in the formation of OH[–] and MgH⁺ surface groups.

Theoretical and experimental studies have established a qualitative correlation between the chemical properties of the surface Mg–O pairs and their coordination numbers: hydrogen adsorption energy,^{14–16} hydrogen desorption temperature,^{11–13,17} and vibrational frequencies of the OH[–] groups^{1,18} decrease in the sequence Mg(3C)–O(3C) > Mg(4C)–O(3C) > Mg(4C)–O(4C), while ionicity^{14,16,19,20} and surface exciton energy^{21,22} increase in the same order. The explanation of these correlations was based on the observation that surface sites with lower coordination numbers usually have lower Madelung constants. This results in lower band gap and ion charges. Enhanced covalency of the low-coordinated sites in its turn favors electron transfer from the bonding σ orbital of the hydrogen molecule to the surface and from the surface to the antibonding σ^* orbital, cleavage of the H–H bond, and formation of stronger O–H and Mg–H bonds, as described in previous studies.^{16,23}

Although the use of such a simple geometrical parameter as a coordination number was very helpful for qualitative analysis of experimental and theoretical data, results of sev-

eral experiments^{1,13,18,24} and calculations^{16,20} suggest that there is no perfect correlation “coordination number—chemical properties.” According to the discussion above, this can be explained by the fact that due to the long range character of the electrostatic potential, coordination number (local structure) does not determine unambiguously the Madelung constant of a particular site.

In this paper we address the following question: is it possible to find another simple parameter, instead of coordination number, which correlate better with chemical properties of the low-coordinated surface sites? In the following section we speculate that parameters ΔF_{O} and ΔF_{MgO} (defined as combinations of Madelung constant of surface ions) should correlate with oxygen charge, and characteristics of hydrogen adsorption on the MgO surface, respectively. By performing *ab initio* pseudopotential calculations of hydrogen adsorption on nine low-coordinated MgO surface sites with different values of the ΔF_{O} and ΔF_{MgO} parameters, as described in Sec. III, we showed that charges and reactivity are not determined by the coordination number alone. In particular, we found that sites with the same coordination numbers have different charges and reactivities with respect to hydrogen chemisorption, depending mainly on their corresponding ΔF_{O} and ΔF_{MgO} parameters.

II. THEORETICAL METHOD

A reduction in the ionic charge of low-coordinated oxygen ions means that some back-donation of the electronic charge occurs to the neighboring Mg²⁺ ions. This transfer of electron is most likely to occur to the Mg neighbor, having the least negative Madelung potential [ϕ_{Mg} (max)] among all nearest neighbors of oxygen. Therefore, it is natural to correlate the oxygen ionic charge with the value

$$\Delta F_{\text{O}} = \phi_{\text{O}} - \phi_{\text{Mg}}(\text{max}). \quad (1)$$

Similarly, it is natural to correlate the structure and adsorption energy of H₂ chemisorption with the parameter

$$\Delta F_{\text{MgO}} = \phi_{\text{O}} - \phi_{\text{Mg}}, \quad (2)$$

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characteristic for the $\text{Mg}^{2+}-\text{O}^{2-}$ low-coordinated adsorption site.

To define parameters ΔF_{O} and ΔF_{MgO} , we use “ideal” Madelung constants ϕ_{O} and ϕ_{Mg} for an unrelaxed lattice of point charges. Of course, many other factors (such as ionic relaxation,²⁵ noninteger charges of surrounding ions,²⁶ gradient of the surface potential,^{25,27} etc.) may influence surface ionicity and adsorption properties. However, we believe that these factors are also correlated with ΔF_{O} and ΔF_{MgO} , thus correlations “ ΔF_{O} —oxygen charge” and “ ΔF_{MgO} —reactivity” may not be destroyed. An important advantage of using the “ideal” Madelung constants is that these parameters can be easily computed for each low-coordinated surface site of interest using a method described in Ref. 28 (also see Refs. 21 and 24) and Madelung potentials from periodic (flat surface, step, edge, etc.) structures calculated by the Ewald summation formulas.

For calculations of the electronic structure and adsorption properties of the MgO surface low-coordinated sites, we employed the Embedded Cluster model developed earlier for

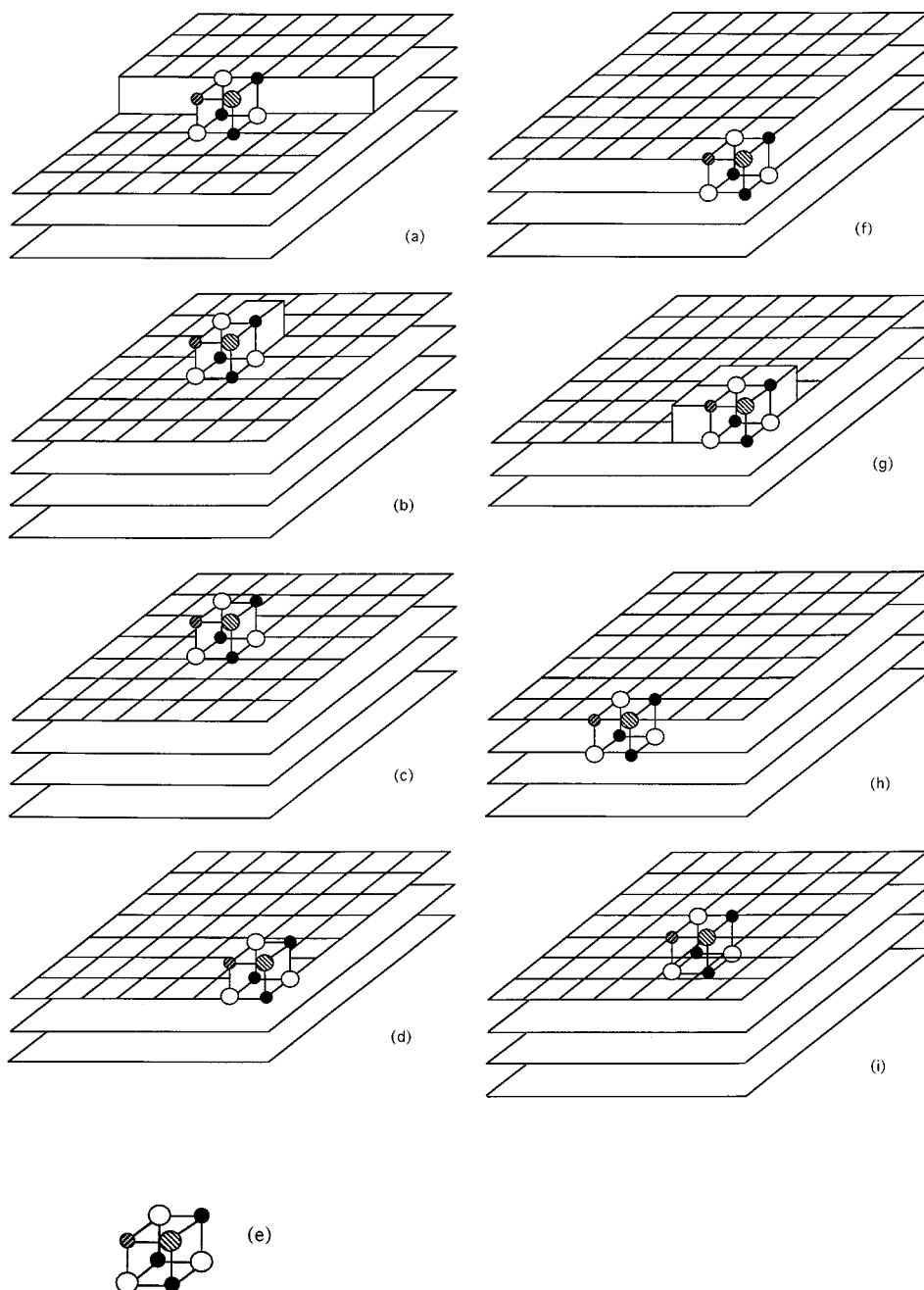


FIG. 1. Models of the MgO surface low-coordinated sites employed in the present study: (a) MgO molecule attached to the surface step; (b) cluster Mg_3O_3 on the (001) surface; (c) cluster Mg_2O_2 on the (001) surface; (d) cluster Mg_2O_2 on the corner; (e) free Mg_4O_4 cluster; (f) corner; (g) cluster Mg_4O_5 on the corner; (h) edge; and (i) (001) surface. In all cases, the quantum cluster was the Mg_4O_4 cube, and the H_2 molecule was adsorbed on shaded Mg—O pairs. All other ions were described by whole-ion pseudopotentials.

TABLE I. Parameters ΔF_{MgO} and H_2 adsorption energies (kcal/mol) on low-coordinated sites on the MgO crystal surface.

Surface site	Fig.	CN ^a		ΔF_{MgO}		Adsorption energy	
		Mg	O	Our model	“exact”	Unrelaxed	Relaxed
MgO near step	1(a)	3	3	2.342	2.361	160.9	131.7
Island Mg_3O_3 on the (001) surface	1(b)	3	3	2.614	2.614	91.7	56.9
Island Mg_2O_2 on the (001) surface	1(c)	3	3	2.720	2.719	74.0	48.6
Island Mg_2O_2 on the corner	1(d)	3	3	2.852	2.827	48.2	12.4
Free Mg_4O_4 cluster	1(e)	3	3	2.912	2.912	29.7	13.2
Corner	1(f)	4	3	3.016	2.994	5.9	3.8
Island Mg_4O_5 on the corner	1(g)	4	3	3.080	3.055	1.5	1.3
Step	1	4	4	3.190	3.182	no adsorption	
(001) surface	1(i)	5	5	3.362	3.363	no adsorption	

^aCN stands for coordination numbers of the reactive Mg–O pairs.

studying the electronic and geometrical structure of bulk and surface defects in ionic crystals.^{29–31} Similar models were recently employed for studying bulk $[\text{Li}^+\text{O}^-]$ ³² and Cu^{2+} , Ag^{2+} (Ref. 33) defects in MgO crystals and adsorption of CH_4 ^{26,34} and CO molecules³⁵ on the MgO surface.

In the Embedded Cluster model, crystal with point defect (adsorbate) is divided into *quantum cluster* (or *cluster*) and the *surrounding lattice*. The cluster consists of the adsorbate and nearest lattice sites, and is treated by the restricted Hartree–Fock molecular orbital method, taking into account the embedding potential from the surrounding lattice, as described below. For a better comparison of properties of different low-coordinated sites, we choose the same quantum cluster Mg_4O_4 (Fig. 1) for all surface sites considered here. To reduce the computational demand, we approximated the atomic cores in the cluster by the Stevens–Basch–Krauss, effective core potential,³⁶ and used the CEP-31G basis set for the valence electrons. We studied geometries and energetics of dissociative adsorption of hydrogen on both unrelaxed and relaxed surface sites (the Mg–O pairs on which H_2 molecule is adsorbed are shaded in Fig. 1). In the relaxed case, coordinates of the three-coordinated surface ions were optimized, while all other lattice atoms fixed. The GAUSSIAN92 computer code³⁷ was used in all calculations.

Several approximations were made for the embedding potential of the surrounding lattice on the cluster. The surrounding lattice was modeled by a finite (188–252 ions) array of ions (Fig. 1) at the fixed MgO lattice sites, with the experimental lattice constant of 2.106 Å. These ions were represented by whole-ion pseudopotentials. Similar to previous works,^{29,38,39} we used the effective core potential³⁶ for cations and point charge ($q = -2.0$) potential for anions. Thus, we ignored the lattice relaxation and electronic density redistribution outside of the cluster. For our study, we selected nine low-coordinated sites [Figs. 1(a)–1(i)] on the MgO surface, having Madelung constants varying from 1.181 to 1.682. The low limit corresponds to a MgO molecule attached to the surface step, as shown in Fig. 1(a) and the high limit to the (001) surface, as shown in Fig. 1(i). The free Mg_4O_4 cluster as shown in Fig. 1(e) has an intermediate value of 1.456 for the Madelung constant. This selection allows us to study correlations between chemical properties

with a wide range of Madelung constants. We found that with our choice of size and shape of the surrounding lattice for each surface site, the parameter ΔF_{MgO} has errors less than 1% with respect to its “exact” value for an infinite lattice of point charges (see Table I). This accuracy is satisfactory for our purposes.

III. RESULTS AND DISCUSSION

To check accuracy of the approximations involved in the Embedded Cluster model, we compared results of four test calculations for coadsorption of MgO and H_2 molecules on the MgO(001) surface modeled by the 8^*8^*4 lattice with different choices of quantum clusters and basis sets. First, we performed the all-electron calculation of cluster $\text{Mg}_3\text{O}_3(+\text{H}_2)$ shown in Fig. 2, using the 6-31G split valence basis set augmented with *sp* diffuse functions on oxygen and hydrogen atoms.⁴⁰ All remaining ions of the 8^*8^*4 lattice were modeled by the whole-ion pseudopotentials, as described above. The geometry of the Mg_3O_3 cluster was optimized first and then kept constant during the structural optimization of the adsorbed H_2 molecule. Geometrical parameters of the MgO– H_2 coadsorption complex and H_2 binding energy are listed in the first column of Table II. These results are used as a reference point in our study, and are in a qualitative accord with the geometry optimized using the semiempirical Embedded Cluster model¹⁴ as listed in the last column of Table II. Errors (in Å and kcal/mol) produced by three more approximate treatments are listed in the 2–4

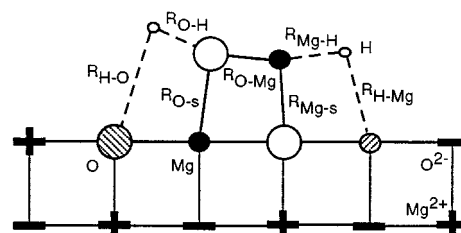


FIG. 2. $\text{Mg}_3\text{O}_3+\text{H}_2$ and $\text{Mg}_2\text{O}_2+\text{H}_2$ clusters used for calculations of MgO and H_2 coadsorption on the MgO(001) surface.

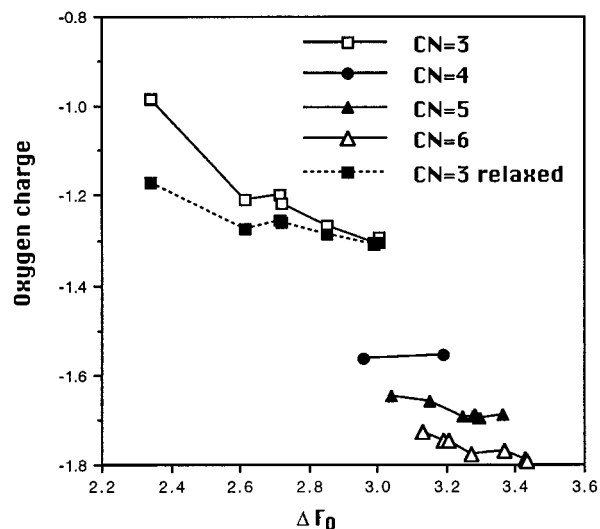
TABLE II. Bond distances (\AA) and H_2 adsorption energy (kcal/mol) for coadsorption of H_2 and MgO molecules on the $\text{MgO}(001)$ surface.^a

Cluster	$\text{Mg}_3\text{O}_3+\text{H}_2$		$\text{Mg}_2\text{O}_2+\text{H}_2$		Ref. 14 INDO
	AE	VA	VA	AE	
$R_{\text{O}-s}$	2.34	0.05	0.07	-0.02	2.21
$R_{\text{Mg}-s}$	2.07	0.14	0.15	-0.02	2.15
$R_{\text{O}-\text{Mg}}$	1.76	0.02	0.02	0.00	1.91
$R_{\text{Mg}-\text{H}}$	1.75	0.00	0.00	0.00	1.30
$R_{\text{H}-\text{Mg}}$	2.64	0.16	0.18	0.09	...
$R_{\text{O}-\text{H}}$	0.94	0.00	0.00	0.00	0.93
$R_{\text{H}-\text{O}}$	2.95	0.00	0.00	-0.06	...
E_{ads}	118.2	-1.6	-1.2	0.2	...

^aIn the first column are results from the most accurate all-electron (AE) calculations for the $\text{Mg}_3\text{O}_3+\text{H}_2$ cluster. Columns 2-4 show errors produced by reducing the size of cluster to $\text{Mg}_2\text{O}_2+\text{H}_2$ and/or using a valence approximation (VA). For comparison, the last column gives the bond distances from INDO calculations by Shluger *et al.*¹⁴

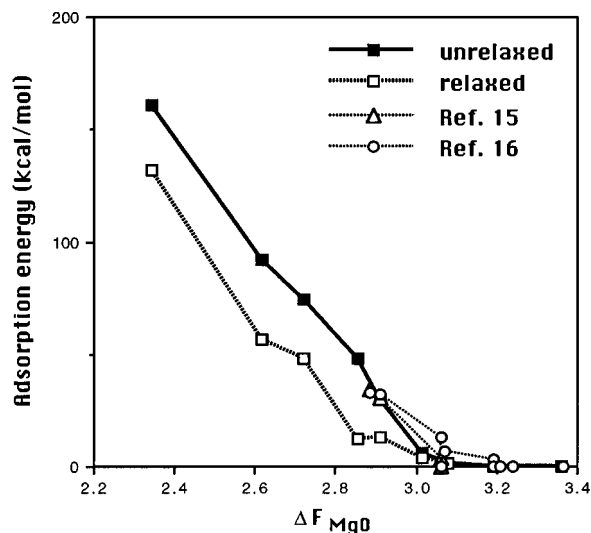
columns of Table II. The second column contains results obtained with the pseudopotential description of atomic cores in the $\text{Mg}_3\text{O}_3(+\text{H}_2)$ cluster and the CEP-31G basis set for the valence electrons. This approximation overestimates the $R_{\text{Mg}-s}$ and $R_{\text{H}-\text{Mg}}$ bond lengths by 0.14 and 0.16 \AA , respectively, and underestimates the H_2 binding energy by 1.6 kcal/mol. These errors do not change substantially, i.e., 0.15 and 0.18 \AA for the $R_{\text{Mg}-s}$ and $R_{\text{H}-\text{Mg}}$ bonds, respectively, and 1.2 kcal/mol for the binding energy, as listed in the third column in Table II for the case, where the smaller cluster $\text{Mg}_2\text{O}_2(+\text{H}_2)$ was used, in which the two surface ions (shaded in Fig. 2) were treated as part of the surrounding lattice and represented by whole-ion pseudopotentials. Comparing with the fourth column, where the cluster $\text{Mg}_2\text{O}_2(+\text{H}_2)$ was computed using the all-electron basis set, the errors are smaller than those produced by the valence approximation. Thus, we can conclude that the whole-ion pseudopotential representation of the surrounding lattice produces smaller errors than the valence approximation inside the cluster and the omission of diffuse functions in the basis sets for oxygen and hydrogen atoms.

Mulliken charges of oxygen ions categorized by their coordination numbers at the nine low-coordinated unrelaxed surface sites are plotted in Fig. 3 as functions of the parameter ΔF_{O} . We found that 6-, 5-, and 4-coordinated oxygen species have an electronic configuration close to O^{2-} . This is in qualitative agreement with previous studies,^{14,16,20,41-43} though a quantitative comparison between our present results with those from these previous studies is not possible, since different models and basis sets were used. Charge variations correlate well with the coordination number. In particular, the oxygen charges at sites with coordination numbers from 4 to 6 are nearly independent with respect to ΔF_{O} . However, charges of the 3-coordinated oxygen ions change from -1.0 to -1.3 as ΔF_{O} increases from 2.342 to 3.080. Smaller variation was found if these sites are relaxed. Note that at the low ΔF_{O} values, i.e., $\Delta F_{\text{O}}=2.342$, corresponding to the MgO molecule adsorbed near the surface step as in Fig. 1(a), the Madelung potential is not sufficient to localize two electrons on the oxygen atom, consequently, the Mg and O sites

FIG. 3. Mulliken charges of the oxygen ions in Mg_4O_4 quantum cluster plotted as functions of the parameter ΔF_{O} .

may have a radical-like electronic environment similar to a free diatomic $\text{Mg}^{+1}\text{O}^{-1}$ molecule.^{14,26} Similar results were also obtained for magnesium ions: 6-, 5-, and 4-coordinated sites are almost doubly charged, while charges of 3-coordinated Mg ions vary from +0.8 to +1.3, in correlation with the Madelung constant of the site.

As discussed in the Introduction, the lowering of ionicity at the sites with low-coordination numbers and Madelung constants, corresponds to the increase of the chemical reactivity. The relationship between the energy of H_2 adsorption on the unrelaxed sites and the ΔF_{MgO} parameter is shown in Fig. 4 and also listed in Table I. We found that the H_2 adsorption energy decreases from 160.9 kcal/mol to about zero almost linearly as ΔF_{MgO} increases from 2.342 up to about

FIG. 4. Adsorption energy of H_2 molecule on MgO low-coordinated sites (difference between energy of the adsorption complex and the sum of energies of separated cluster and a free H_2 molecule) as functions of the ΔF_{MgO} parameter. Results of Kobayashi *et al.*¹⁶ and Anchell *et al.*¹⁵ are also plotted for comparison.

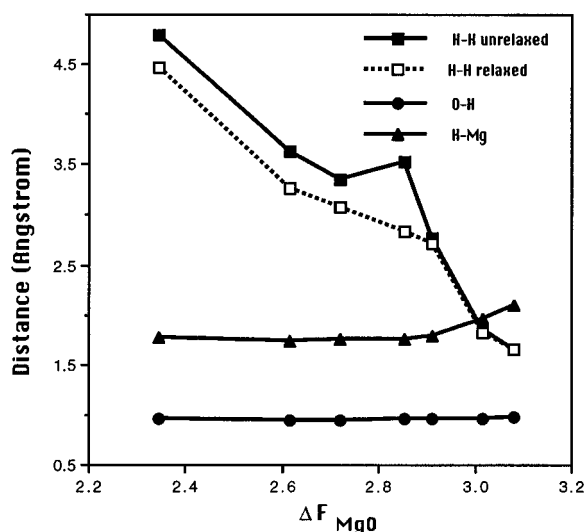


FIG. 5. Geometrical parameters of H_2 adsorption on MgO low-coordinated sites as functions of the ΔF_{MgO} parameter.

3.1. There is no stable adsorption of hydrogen on the edge [Fig. 1(h)] and (001) surface⁴⁴ [Fig. 1(i)], where the ΔF_{MgO} parameters are 3.190 and 3.362, respectively. For these sites, the calculated adsorption energies are smaller than the basis set superposition error (0.9 kcal/mol) computed using the full counterpoise method. The most reactive sites are the $\text{Mg}(3\text{C})\text{--O}(3\text{C})$ surface sites. For these sites, the H_2 adsorption energy varies from 29.7 to 160.9 kcal/mol, in good correlation with the value of ΔF_{MgO} parameter. This is a clear evidence that the Madelung constants are important parameters determining the reactivity of the low-coordinated MgO surface sites.

Higher chemical activity of sites with lower Madelung constants is reflected also in the behavior of the geometrical parameters of H_2 adsorption as functions of the ΔF_{MgO} parameter, as shown in Fig. 5. Both $\text{Mg}\text{--H}$ and $\text{O}\text{--H}$ bond lengths decrease if ΔF_{MgO} decreases, though less markedly for the $\text{O}\text{--H}$ bond. Generally, shorter bonds correspond to higher stretching vibrational frequencies, thus, our results confirm the earlier conclusions regarding positive shift of infrared adsorption spectra of low-coordinated surface OH^- groups.^{1,18} The $\text{H}\text{--H}$ distance shows the most appreciable variation from 0.73 Å (this value is characteristic for the free H_2 molecule) for H_2 molecule near the flat (001) surface and edge [Figs. 1(i) and 1(h), respectively] to 4.8 Å corresponding to the complete breaking of the $\text{H}\text{--H}$ bond for the H_2 adsorption on the MgO molecule attached to the surface step [Fig. 1(a)]. Thus, the bond distances are in good correlation with the values of parameter ΔF_{MgO} . This is consistent with the behavior of surface ions charges and H_2 adsorption energy, as discussed above.

Next, we studied atomic relaxation of the low-coordinated surface sites. Equilibrium structure of the free Mg_4O_4 cluster [Fig. 1(e)] was found to be a distorted cube. The $\text{Mg}\text{--O}\text{--Mg}$ and $\text{O}\text{--Mg}\text{--O}$ angles have values of 87.4° and 92.6°, respectively. These values are close to their “cubic” values of 90.0°. The $\text{Mg}\text{--O}$ distance of 1.965 Å is smaller than in the MgO crystal, in agreement with previous

all-electron calculations.²⁰ No “dimerization” was found in our calculations, in contrast with the results of tight binding method reported earlier.⁴⁵ An oxygen ion at the corner [Fig. 1(f)] relaxes inward, in agreement with rounding of the corner effect predicted previously.^{46,47} However, this relaxation of 0.13 Å is smaller than 0.31 Å, which was computed by the atomistic lattice simulation technique.⁴⁶

Generally, atomic relaxation shifts 3-coordinated ions to the position with a higher Madelung potential,⁴⁸ increases absolute values of their charges, as shown in Fig. 3 (broken line) and therefore decreases the chemical activity of defects (Table I and broken lines in Figs. 4 and 5). In our calculations, the variation of charge of the 4-, 5-, and 6-coordinated ions are much smaller than in the 3-coordinated case and may have either directions depending on the particular defect structure (also see Ref. 19).

IV. CONCLUSIONS

Results presented above allow us to conclude that $\text{Mg}(3\text{C})\text{--O}(3\text{C})$ surface pairs on the MgO crystal surface have appreciable reactivities toward dissociative adsorption of hydrogen molecules. However, surface pairs with the same coordination numbers may have different properties. We found that ionicity and chemical reactivity of the MgO low-coordinated sites are in good correlation with the combinations ΔF_{O} and ΔF_{MgO} of Madelung constants on these sites: surface 3-coordinated oxygen ions with lower values of the parameter ΔF_{O} have lower charges; surface $\text{Mg}\text{--O}$ pairs with lower values of ΔF_{MgO} bind hydrogen more strongly and dissociate hydrogen molecules more readily. Since Madelung constants of arbitrary (unrelaxed) low-coordinated site can be easily found without performing expensive calculations of its electronic and geometrical structures, one can roughly estimate the charge distribution and parameters of hydrogen chemisorption for each particular defect site simply interpolating data in Figs. 4–6 from our present study. More theoretical and experimental work, however, is needed in order to confirm the established correlations “Madelung constants—chemical properties” on interaction of the MgO surface with other molecules, as well as on chemical properties of other ionic crystal surfaces.

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¹T. Shido, K. Asakura, and Y. Iwasawa, *J. Chem. Soc. Faraday Trans. I* **85**, 441 (1989).

²E. Knözinger, K.-H. Jacob, and P. Hofmann, *J. Chem. Soc. Faraday Trans.* **89**, 1101 (1993).

³T. Shido, K. Asakura, and Y. Iwasawa, *J. Catal.* **122**, 55 (1990).

⁴T. Ito and J. H. Lunsford, *Nature* **314**, 721 (1985).

⁵D. J. Driscoll, W. Martir, J.-X. Wang, and J. H. Lunsford, *J. Am. Chem. Soc.* **107**, 58 (1985).

⁶T. Ito, J.-X. Wang, C.-H. Lin, and J. H. Lunsford, *J. Am. Chem. Soc.* **107**, 5062 (1985).

- ⁷M. Boudart, A. Delbouille, E. G. Derouane, V. Indovina, and A. B. Walters, *J. Am. Chem. Soc.* **94**, 6622 (1972).
- ⁸A. B. Kunz and M. P. Guze, *Chem. Phys. Lett.* **45**, 18 (1977).
- ⁹S. Coluccia, F. Boccuzzi, G. Ghiotti, and C. Morterra, *J. Chem. Soc. Faraday Trans. I* **78**, 2111 (1982).
- ¹⁰S. Coluccia, F. Boccuzzi, G. Ghiotti, and C. Mirra, *Z. Phys. Chem.* **121**, 141 (1980).
- ¹¹T. Ito, T. Sekino, T. Moriai, and T. Tokuda, *J. Chem. Soc. Faraday Trans. I* **77**, 2181 (1981).
- ¹²T. Ito, T. Murakami, and T. Tokuda, *J. Chem. Soc. Faraday Trans. I* **79**, 913 (1983).
- ¹³T. Ito, M. Kuramoto, M. Yoshioka, and T. Tokuda, *J. Phys. Chem.* **87**, 4411 (1983).
- ¹⁴A. L. Shluger, J. D. Gale, and C. R. A. Catlow, *J. Phys. Chem.* **96**, 10 389 (1992).
- ¹⁵J. L. Anchell, K. Morokuma, and A. C. Hess, *J. Chem. Phys.* **99**, 6004 (1993).
- ¹⁶H. Kobayashi, D. R. Salahub, and T. Ito, *J. Phys. Chem.* **98**, 5487 (1994).
- ¹⁷H. Duński, W. K. Jóźwiak, and H. Sugier, *J. Catal.* **146**, 166 (1994).
- ¹⁸E. Knözinger, K.-H. Jacob, S. Singh, and P. Hoffmann, *Surf. Sci.* **290**, 388 (1993).
- ¹⁹E. A. Colbourn, *Surf. Sci. Rep.* **15**, 281 (1992).
- ²⁰J. M. Recio, R. Pandey, A. Ayuela, and A. B. Kunz, *J. Chem. Phys.* **98**, 4783 (1993).
- ²¹E. Garrone, A. Zecchina, and F. S. Stone, *Philos. Mag. B* **42**, 683 (1980).
- ²²A. Zecchina, M. G. Lofthouse, and F. S. Stone, *J. Chem. Soc. Faraday Trans. I* **71**, 1476 (1975).
- ²³H. Kobayashi, M. Yamaguchi, and T. Ito, *J. Phys. Chem.* **94**, 7206 (1990).
- ²⁴E. Giamello, P. Ugliengo, and E. Garrone, *J. Chem. Soc. Faraday Trans. I* **85**, 1373 (1989).
- ²⁵A. L. Shluger, A. L. Rohl, and D. H. Gay (to be published).
- ²⁶K. J. Børve, *J. Chem. Phys.* **95**, 4626 (1991).
- ²⁷M. Causà and F. Ricca, *Surf. Sci.* **298**, 251 (1993).
- ²⁸J. Magill, J. Bloem, and R. W. Ohse, *J. Chem. Phys.* **76**, 6227 (1982).
- ²⁹V. E. Puchin, A. L. Shluger, K. Tanimura, and N. Itoh, *Phys. Rev. B* **47**, 6226 (1993).
- ³⁰V. E. Puchin, A. L. Shluger, and N. Itoh, *Phys. Rev. B* **47**, 10 760 (1993).
- ³¹V. E. Puchin, A. L. Shluger, Y. Nakai, and N. Itoh, *Phys. Rev. B* **49**, 11 364 (1994).
- ³²J. Zuo, R. Pandey, and A. B. Kunz, *Phys. Rev. B* **44**, 7187 (1991).
- ³³J. L. Pascual, L. Seijo, and Z. Barandiarán, *J. Chem. Phys.* **98**, 9715 (1993).
- ³⁴K. J. Børve and L. G. M. Pettersson, *J. Phys. Chem.* **95**, 7401 (1991).
- ³⁵M. A. Nygren, L. G. M. Pettersson, Z. Barandiarán, and L. Seijo, *J. Chem. Phys.* **100**, 2010 (1994).
- ³⁶W. Stevens, H. Basch, and J. Krauss, *J. Chem. Phys.* **81**, 6026 (1984).
- ³⁷M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, *Gaussian 92/DFT, Revision F.2* (Gaussian, Inc., Pittsburgh, PA, 1993).
- ³⁸N. W. Winter, R. M. Pitzer, D. K. Temple, *J. Chem. Phys.* **87**, 2945 (1987).
- ³⁹A. G. Anshits, E. N. Voskresenskaya, V. V. Rivanenkov, V. A. Nasluzov, and K. M. Neiman, *React. Kinet. Catal. Lett.* **46**, 285 (1992).
- ⁴⁰K. Sawabe, N. Koga, K. Morokuma, and Y. Iwasawa, *J. Chem. Phys.* **97**, 6871 (1992).
- ⁴¹M. Causà, R. Dovesi, C. Pisani, and C. Roetti, *Surf. Sci.* **175**, 551 (1986).
- ⁴²I. V. Abarenkov and T. Y. Frenkel, *J. Phys. Condens. Matter* **3**, 3471 (1991).
- ⁴³M. Causà, R. Dovesi, E. Kotomin, and C. Pisani, *J. Phys. C Solid State Phys.* **20**, 4983 (1987).
- ⁴⁴E. A. Colbourn and W. C. Mackrodt, *Surf. Sci.* **117**, 571 (1982).
- ⁴⁵S. Moukouri and C. Noguera, *Z. Phys. D* **24**, 71 (1992).
- ⁴⁶E. A. Colbourn, J. Kendrick, and W. C. Mackrodt, *Surf. Sci.* **126**, 550 (1983).
- ⁴⁷P. W. Tasker and D. M. Duffy, *Surf. Sci.* **137**, 91 (1984).
- ⁴⁸E. A. Colbourn, in *Defects in Solids—Modern Techniques*, edited by A. V. Chadwick and M. Terenzi (Plenum, New York, 1986), p. 337.