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Effect of charge deformation and geometric relaxation on the dynamics and the thermodynamic properties of the MgO (001) surface

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Model calculations by Martin and Bilz have indicated that a slight enhancement of effective surface charges may largely account for recent observations on the static (001) MgO surface (low-energy electron diffraction, electron-energy-loss spectroscopy, and x-ray photoemission spectroscopy). The simplest model incorporating the feature of charge enhancement, a modified rigid-ion model, is used in the present work to study the dynamical and thermodynamic properties of this surface. The results are compared with available experimental data.

INTRODUCTION

Recently the static and the dynamical properties of the MgO (001) surface have been treated theoretically by several authors.[1-3] The study of this surface is of particular interest since of all the rocksalt-structured crystals, MgO is the only case in which there exist experimental data relating to both the statics[4-6] and the dynamics[7] of the surface. This raises the question to which extent it is possible to treat the static relaxation and the dynamics of a surface in a consistent fashion with a single ionic interaction model. A first attempt in this direction was made by Chen and de Wette[1,8] who adapted bulk lattice-dynamical shell models (SM's) to evaluate both the static relaxation effects and the dynamics of the (001) surfaces of various rocksalt-structured ionic crystals. This work showed that these bulk SM's do not lead to convergent results for the static surface relaxation, but that, given a relaxed surface configuration, reasonable agreement between calculated and measured surface-phonon spectrum could be obtained for the MgO (001) surface. More recently, Barnett and Bass[3] used a breathing SM (BSM) to study both the relaxation and the dynamics of the MgO (001) surface. The BSM does lead to convergent relaxation results, and the calculated interlayer spacings in the surface region agree reasonably well with the available low-energy electron diffraction (LEED) data.[4] However, the dynamical results do not seem to be any "better" than those obtained with a simple SM for the unrelaxed[9] and relaxed[10] (001) surfaces of MgO.

The difficulty in judging the dynamical results of these calculations is that there are hardly any experimental results with which they can be compared. This is in the nature of the problem: "Microscopic" surface modes, i.e., modes localized in a few atomic layers near the surface, which are most affected by surface relaxation, have so far escaped experimental detection. On the other hand, "macroscopic" surface modes which penetrate deeply into the crystal, some of which have been detected (e.g., the Fuchs-Kliewer modes) are hardly affected by relaxation, especially at the long wavelengths at which optical experiments are performed. The only experiment providing some test for dynamical results is Rieder and Hörl's[7] neutron scattering determination of the surface-excess frequency distribution of the MgO (001) surface. Because of the importance of this experiment, we mention a few details: The surface-excess frequency distribution $f^s(\omega)$ for a slab-shaped crystal is defined as[9]

$$f^s(\omega)=(N/n)[f^{\mathrm{slab}}(\omega)-f^{\mathrm{bulk}}(\omega)]\,,$$

where f^{slab} and f^{bulk} are the properly normalized frequency distributions of the slab and the bulk; N is the total number of ions in the slab and n the number of surface ions. In general, $f^s(\omega)$ exhibits a succession of peaks and valleys, indicating that the occurrence of surface modes is accompanied by the depletion of an equal number of bulk modes. The importance of $f^s(\omega)$ is that it determines the vibrational contributions to the surface thermodynamic functions of crystals.

The present work builds on a recent study by Martin and Bilz[2] (in the following quoted as MB). These authors have carried out a careful and systematic static relaxation study of the MgO (001) surface, using a variety of ionic interaction models which are all adaptations and modifications of bulk rigid-ion and shell models. The main features of these modifications are: (a) environment-dependent variations in the anion (O^{2-}) polarizability, (b) quadrupole contributions to the total energy of the crystal, (c) charge transfer at the surface. The main conclusion of the work is: ". . . . that a small (≈5%) enhancement of the top-layer effective charges can largely account for the available experimental results on the static properties of (001) MgO." It was further noted that variable polarizability and quadrupole effects do not lead to appreciable improvements in the (static) relaxation results, but that such effects might be important in the treatment of the surface vibrations.

The importance of Martin and Bilz's work is that it gives a detailed analysis of the various changes in ionic interactions taking place at the MgO surface, and that it evaluates the effects of these changes on the stability, geometry, and electronic structure of the static surface. In the present note we report on an initial study of the effects of these modified ionic interactions on the dynamical properties of the MgO (001) surface. Since the main improvement in the agreement with experiment resulted from MB's incorporation of surface charge transfer (antiscreening) in the model interaction, we have, as a first step, concentrated on this modification and investigated its effect on the surface vibrational modes. To facilitate comparison with existing and future experimental results, we have also evaluated the changes in the surface-excess frequency distribution $f^s(\omega)$ and the surface thermodynamic properties.

The present calculations were carried out for a 15-layer MgO (001) slab with models 1 and 4 of MB. Both are rigid-ion models; model 1 takes into account only static relaxation effects, while model 4 incorporates both relaxation and charge-transfer effects. The basic method of calculation is described in Ref. 11; suitable modifications were made to incorporate the enhancement of the effective charges in the top layer. The calculations were carried out for 66 two-dimensional wave vectors in the two-dimensional surface Brillouin zone (SBZ). In order to obtain the surface-excess frequency distribution, corresponding calculations were performed for the bulk (cf. Ref. 1).

RESULTS AND DISCUSSION

The direct dynamical effects of relaxation and charge transfer show up as changes in the individual surface modes. Since most of these modes cannot yet be experimentally observed, we will only briefly summarize the main effects here. In Fig. 1 we display the slab dispersion curves along the three symmetry directions in the SBZ, obtained from the calculations with models 1 and 4. For the sake of brevity we refer the reader to Ref. 9 for the nomenclature adopted for these surface-mode dispersion curves and for a description of the basic characteristics of the particular modes mentioned. The main effects of charge transfer (model 4) as compared to "relaxation only" (model 1) are the following:

(1) The frequencies of the Lucas modes (S_4, S_5) at the zone center are lowered by 24%.

(2) The frequency of the Rayleigh mode (S_1) in $\overline{\Gamma}\overline{X}$ is lowered by 27%.

(3) Owing to the overall lowering of the surface-mode frequencies, along $\overline{X}\overline{M}$ and $\overline{M}\overline{\Gamma}$ near the zone boundary, more surface modes are "peeled off" from the bottom of the acoustic bulk bands (S_6, S_4, S_7).

The question arises whether these drastic changes in the Lucas and Rayleigh modes are direct dynamical effects of charge transfer, or indirect effects, i.e., caused by increased interlayer Born-Mayer interactions resulting from the inward relaxation. The latter possibility seems remote: the changes in the interlayer separations obtained in the SM relaxation calculation of Chen and de Wette[1] are two to three times larger than those obtained with MB's model 4, yet the frequency of the Lucas modes at $\overline{\Gamma}$ (Ref. 1) was not at all sensitive to these interlayer changes. The same is true for the rigid-ion model; comparison of the results of an unrelaxed rigid-ion calculation with those of the MB model-1 calculation shows hardly any change in the Lucas modes. The same observations are true for the Rayleigh mode at $\overline{X}$. This leads to the conclusion that the large shifts in the Lucas modes at $\overline{\Gamma}$ and the Rayleigh mode on $\overline{\Gamma}\overline{X}$ are indeed direct effects of the charge transfer. However, as we will see below, these shifts do not agree with experiment and the question arises whether there are other effects, not taken into account up to this point, which would cause the Lucas and Rayleigh modes to remain more or less unchanged, in spite of the charge transfer. One such effect has been suggested by MB, namely, changes in the $l=0$ intralayer Born-Mayer interactions: these authors point out (Ref. 2, footnote 29) that in the case of the rigid-ion model an increase in the interaction by a factor of 3 causes no changes in the geometry. To assess the effects of such a change on the dynamics, we have repeated the calculations for wave vectors at $\overline{\Gamma}$ and $\overline{X}$ with the following results: By increasing the $l=0$ intralayer repulsive forces by a factor of 3, as was done in the static calculation, the frequency of the Lucas modes at $\overline{\Gamma}$ is increased by a factor of about 4, raising it above the longitudinal optical frequency, i.e., above the bulk bands. At the same time the Rayleigh mode at $\overline{X}$ becomes unstable. Repeating the calculations with increases in the $l=0$ intralayer repulsive forces by factors of 1.5 and 2, respectively, we find a gradual increase in the Lucas-mode frequency at $\overline{\Gamma}$, from its low value caused by the charge transfer. The frequency of the Rayleigh mode at $\overline{X}$ initially in-

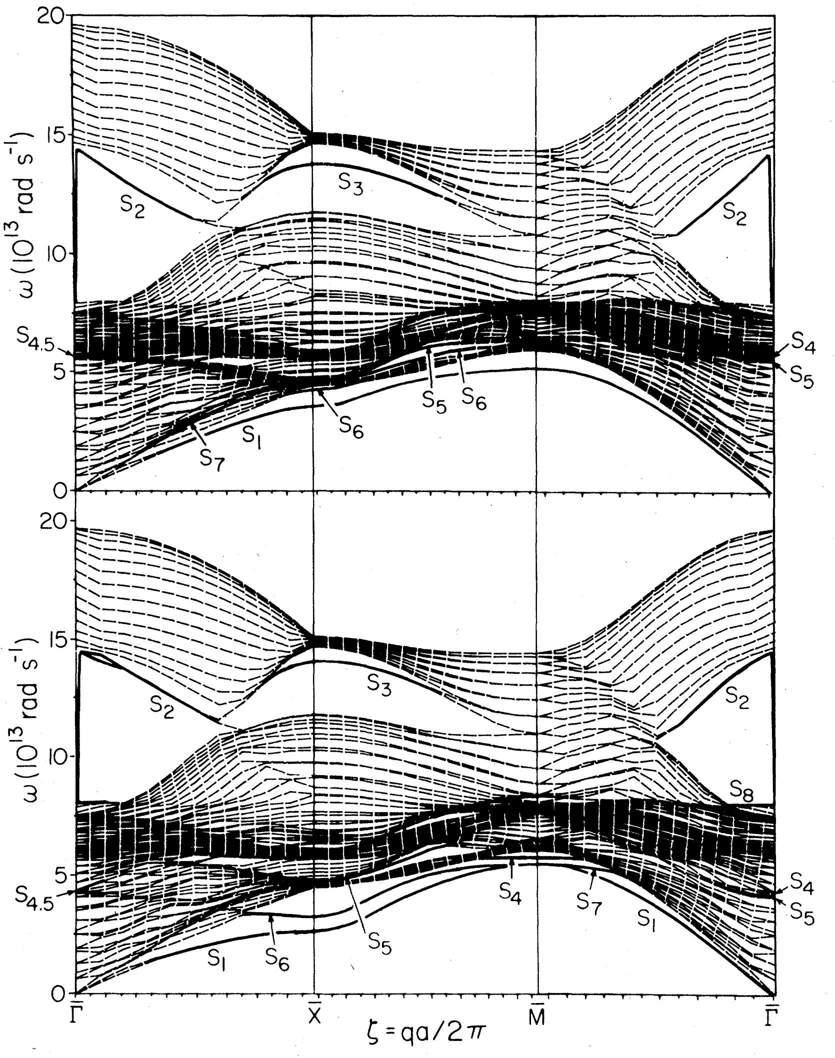

FIG. 1. Dispersion curves of a 15-layer MgO (001) slab along symmetry direction in the SBZ, calculated with models 1 and 4 of MB. For a description of the surface modes S_i, refer to Ref. 9.

creases with increasing strength of repulsive intralayer interaction, maintaining its polarization character, but losing its pure surface-mode character. However, with further increase of the interaction, the mode becomes unstable. These results indicate that the dynamic properties, unlike the static ones, are extremely sensitive to changes in the intralayer repulsive interactions. However, there exists no consistent, *a priori* way to determine if and by how much the $l=0$ intralayer interaction should be increased to arrive at the correct results for both the Lucas and Rayleigh modes. It is hoped that future experimental results on the Lucas and Rayleigh modes will clarify the situation. In the absence of such results we limit the subsequent discussion to the effects of charge transfer proper.

In Fig. 2 we display the surface-excess frequency distribution $f^s(\omega)$ for the unrelaxed SM calculation of Chen *et al*[9] [panel (a)], and for models 1 and 4 [panels (b) and (c), respectively]; the experimental curve of Rieder and Hörl[7] is displayed in each of the panels. The unrelaxed SM calculation [panel (a)] reproduces the experimental[7] $f^s(\omega)$ quite well, except for the experimental high-frequency peak. The origin of this peak is still being debated and could be due to the presence of hydroxyl ions on the surface (cf. Ref. 9).

Turning now to the present results, we should remember that rigid-ion models give incorrect results for the high-frequency longitudinal-optical modes, so that we should consider only the lower part of the spectrum. Concentrating on peaks I

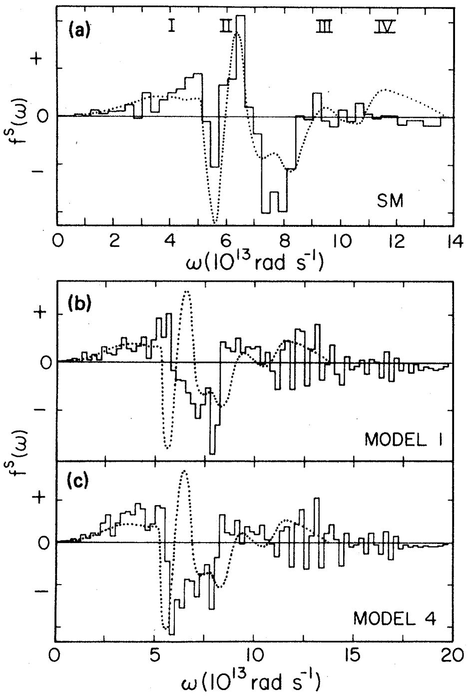

FIG. 2. Surface-excess frequency distribution $f^s(\omega)$ of MgO (001): (a) for the unrelaxed SM; (b) and (c) for models 1 and 4 of MB, respectively. The dotted curve is the experimental $f^s(\omega)$ of Ref. 7. Note the difference in ω scale between panel (a) and panels (b), (c).

and II in the experimental spectrum, we see that the present calculations do not reproduce these peaks nearly as well as did the unrelaxed SM calculation; in fact, peak II is absent. The reason for this is that the Lucas modes, which give rise to this peak in the unrelaxed SM and in experiment, have been lowered so much that peak II has merged with peak I, which is due to the acoustic surface modes.

The determination of $f^s(\omega)$ by neutron scattering as carried out by Rieder and Hörl[7] is a difficult experiment, requiring access to a high-flux research reactor. Considerably simpler are caloric measurements of the surface-excess thermodynamic properties. Since these properties are completely determined by $f^s(\omega)$, a comparison of calculated and measured properties will conceivably shed some light on some of the features of $f^s(\omega)$. Although only a few surface thermodynamic measurements have been made to date, and although their reliability has suffered from ambiguities in surface-area determinations,[12] one can expect more reliable measurements to become available in the future. For this reason we thought it worthwhile to evaluate the surface-excess specific heat C_v^s of MgO (001) for the interaction models discussed here, and to compare the results with earlier results for this quantity. For the definition and a discussion of C_v^s we refer to the work of Chen *et al.*[12] Here we merely mention that C_v^s is zero at zero and high temperatures and has a peak at low temperatures with a maximum at temperature $T\,(C^s_{\max})$, somewhere in the range $0.08\,\Theta_0 - 0.16\,\Theta_0$ (Θ_0 is the bulk Debye temperature). It turns out that for temperatures of interest, i.e., for most of the peak in C_v^s, practically the entire contribution to C_v^s comes from frequencies in peak I of $f^s(\omega)$.

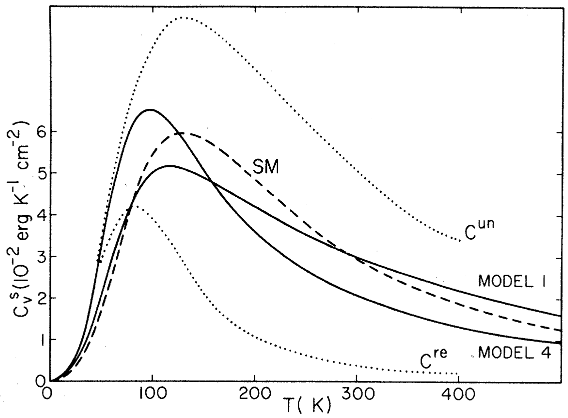

FIG. 3. Surface-excess specific heat C_v^s of MgO (001), calculated with various models: the unrelaxed SM, models 1 and 4 of MB, and the rigid-ion cluster calculation (C^{un}, C^{re}; Ref. 13).

In Fig. 3 we show C_v^s as calculated with models 1 and 4, to the unrelaxed SM result,[12] as well as the results for an unrelaxed and a relaxed 180-ion cluster (Chen *et al.*[13]). It is seen that the models 1, 4, and SM results are fairly close together and are bracketed by the cluster results (C^{un} and C^{re}). The differences between these curves are all due to differences in peak I and the first depletion valley of the corresponding excess density-of-states functions $f^s(\omega)$ (Fig. 2). However, we see that rather significant differences in $f^s(\omega)$ [compare Fig. 2(a) with Figs. 2(b) and 2(c)] are washed out in C_v^s. We therefore have to conclude that measurements of C_v^s are of very limited value to shedding light on the dynamics of the surface.

SUMMARY

Martin and Bilz[2] have shown that LEED, EELS, and XPS data on the MgO (001) surface can be reasonably accounted for with a rigid-ion model incorporating a small enhancement of surface charges. However, as we have found in this work, the dynamical predictions of such a model agree poorly with experiment. They also differ substantially from the results of Chen *et al*[9] using an unrelaxed simple SM and those of Barnett and

Bass[10] using a relaxed BSM, which suggests that the influence of polarizability on the dynamics cannot be neglected. The next step is to perform calculations with some of the modified SM's, proposed by MB,[2] again evaluating the effects of charge enhancement on the surface dynamics, as MB have surmised. This is of particular interest since a volume-dependent polarizability can, under certain conditions, give rise to static[2] and dynamic[3] instabilities. These calculations are presently underway. In conclusion, a unified account of both the static and the dynamic properties of the MgO (001) surface needs substantial further work.

Note added in proof. Instead of "charge transfer" read "charge enhancement" in the text of this paper. In a number of places we refer to the "Rayleigh mode on $\overline{\Gamma X}$" or "... at $\overline{X}$." In these instances we mean the surface mode pair S_1. On the interval $\overline{\Gamma X}$ S_1 has shear horizontal (SH) polarization character and is therefore not a Rayleigh mode, which has sagittal-plane (SP) polarization. Only on the interval $\overline{\Gamma M}$, where it has SP polarization, is S_1 the Rayleigh mode.

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