

Electron–phonon interaction in magnesium: From the monolayer to the Mg(0001) surface

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Available online 4 May 2007

Abstract

We report *ab initio* study of the electron–phonon coupling in a free standing magnesium monolayer and at the Mg(0001) surface. The calculations were carried out using a linear-response approach in the plane-wave pseudopotential representation. Eliashberg spectral function $\alpha^2 F(\omega)$ averaged over electron states at the Fermi surface is presented for the monolayer while for the Mg(0001) surface, we compute the electron–phonon spectral function $\alpha^2 F_{\mathbf{k},i}(\omega)$ for surface states at the $\bar{\Gamma}$ and \bar{M} points.

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Keywords: Two-dimensional structures; Surface dynamics; Electron–phonon coupling

1. Introduction

During the last decade enormous progress in the study of electron and hole dynamics at metal surfaces has been achieved both theoretically and experimentally [1–8]. Interest in this study is motivated by an essential role which electron excitations play in many chemical and physical phenomena. On the other hand, systems with two-dimensional translation symmetries have been extensively studied for a variety of different phenomena, today it is well known that the effect of reducing the dimensionality of a system can change dramatically its properties. This is why a better understanding of surfaces and, in particular, of monolayers, may be very helpful whenever we describe materials with a clear layered structure. The electron–phonon interactions produce a finite phonon lifetime as well as contribute to final lifetimes of excited electrons and holes. They

are responsible for the enhancement of the effective electron mass as it is measured in experiments of electronic heat capacity [9].

In the present work, we have studied the relevance of the electron–phonon interaction in a magnesium monolayer. A similar analysis has been done for a slab of eleven atomic layers of Magnesium that mimics the Mg(0001) surface. In these systems transversal surface phonon modes play a crucial role in the coupling. In fact, for surfaces, the coupling with surface state electrons is normally very efficient and it can suppose the major part of the total contribution to the coupling. In the case of the surface, we compare our value for the mass enhancement parameter λ of the surface state at $\bar{\Gamma}$ point $\lambda_{\bar{\Gamma}} = 0.28$, with experimental photoemission measurements finding an excellent agreement.

2. Theory

E–ph coupling is described by the matrix elements that relate the electron transition from an initial electronic state (i) to a final state (f) through the absorption (emission) of a phonon [9].

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$$g_{\mathbf{q}}(\mathbf{k}, i, f) = \sqrt{\frac{\hbar}{2M\omega_{\mathbf{q}}}} \langle \psi_{f, \mathbf{k}+\mathbf{q}}^0 | \hat{\epsilon}_{\mathbf{q},v} \cdot \delta V_{\mathbf{q}}^{scf} | \psi_{i, \mathbf{k}}^0 \rangle \quad (1)$$

We may now define the electron state dependent Eliashberg function $\alpha^2 F_{\mathbf{k},i}(\omega)$. This function *measures* the effectiveness of phonons of energy $\hbar\omega$ to scatter an electron in a selected initial state $\epsilon_{\mathbf{k},i}$:

$$\alpha^2 F_{\mathbf{k},i}(\omega) = \sum_{\mathbf{q},v,f} \delta(\omega - \omega_{\mathbf{q},v}) |g(\mathbf{k}_i, \mathbf{k}_f, \mathbf{q}, v)|^2 \delta(\epsilon_{\mathbf{k},f} - \epsilon_{\mathbf{k},i}). \quad (2)$$

When initial and final electronic states remain on the Fermi surface ($\epsilon_{\mathbf{k},i} = \epsilon_{\mathbf{k},f} = E_F$), a function averaged over the Fermi surface can be defined by considering the sum over all the possible initial electron states [10].

$$\alpha^2 F(\omega) = \sum_{\mathbf{q},v} \frac{\delta(\omega - \omega_{\mathbf{q},v})}{N(E_f)} \sum_{\mathbf{k},i,f} |g(\mathbf{k}_i, \mathbf{k}_f, \mathbf{q}, v)|^2 \times \delta(\epsilon_{\mathbf{k},i} - E_F) \delta(\epsilon_{\mathbf{k},f} - E_F) \quad (3)$$

For both spectral functions, we calculate a dimensionless parameter λ that gives the strength of the electron-phonon coupling

$$\lambda = 2 \int_0^{\omega_m} \frac{\alpha^2 F(\omega)}{\omega} d\omega. \quad (4)$$

3. Results and discussion

All calculations presented here were performed using the density-functional perturbation theory [11] and the PWSCF code [12]. For the description of the electron-ion interaction in Mg atoms we used a nonlocal norm-conserving pseudopotential with nonlinear core corrections and a plane-wave basis. A periodically repeated slab geometry with Mg(0001) slabs of 11 atomic layers separated by a vacuum region of 18 Å was used to study the surface electronic structure, phonon spectrum and e-ph interaction. The monolayer was also evaluated in the supercell approach where Mg(0001) monolayers were separated by 18 Å of vacuum. Convergence criteria were achieved using energy cutoffs of 32 Ry in the case of the slab and 40 Ry for the monolayer. The number of phonon modes considered in the integrations over the irreducible Brillouin zone (IBZ) were over 90q vectors for the slab and 120 for the monolayer.

In order to obtain the correct phonon and electronic spectrum, atomic positions were fully relaxed for both, the monolayer and for the 11-layer Mg(0001) film. The minimum energy of the monolayer is reached with a lattice parameter in the hexagonal geometry of $a = 5.68$ a.u., which is a $\sim 6\%$ smaller than the corresponding value for the bulk ($a = 5.915$ a.u.). In the case of the Mg(0001) slab, the atomic positions inside the plane maintain the hexagonal symmetry of the bulk and the energy minimization was performed allowing the variation of the interlayer distances. The calculation led to the expansion of the first

and second interlayer spacings of: $\Delta d_{12} = +1.6\%$ and $\Delta d_{23} = +0.3\%$ with respect to bulk interlayer distance. These results are in agreement with other *ab initio* calculation performed by Wright et al. [14] ($\Delta d_{12} = +1.5\%$ and $\Delta d_{23} = +0.5\%$) and experimental measurements of Sprunger et al. [13] ($\Delta d_{12} = (+1.9 \pm 0.3)\%$ and $\Delta d_{23} = (+0.8 \pm 0.4)\%$).

Fig. 1 shows the computed electron bands of both systems along the symmetry directions of the IBZ. All energies are referred to the Fermi level. Electronic structure of the monolayer is shown in the top panel and should be noted that near the center of the IBZ there is a p_z -like occupied band that together with the s-like band will lead to an important contribution to the *e-ph* coupling. In the bottom panel corresponding to electronic states of the surface, dashed lines represent surface states at the $\bar{\Gamma}$ and \bar{M} points with energies relative to the Fermi level of -1.69 eV and -0.98 eV, respectively. These results are in good agreement with recent photoemission experiments [15] where the energy values of -1.63 ± 0.06 and -0.95 ± 0.05 for these surface states have been reported.

To calculate the Eliashberg function and λ , in addition to the electronic structure, we need to know the complete phonon spectrum of both systems. These spectra are shown in the inset panels of Figs. 2 and 3. One can see that for the monolayer, Fig. 2, there exists a soft transverse mode which corresponds to atomic vibrations in the z direction perpendicular to the atomic plane. Such shallow behaviour of the mode, not present in bulk, is due to the broken bonds in this direction. On the other hand, maximum energies of phonons corresponding to inplane vibrations, are higher than those of the bulk. The energy minimization led us to a smaller lattice parameter which produces a stronger interaction between atoms and thus, higher energies of phonons. In Fig. 2 we have also included the phonon density of states $F(\omega)$ together with the Eliashberg

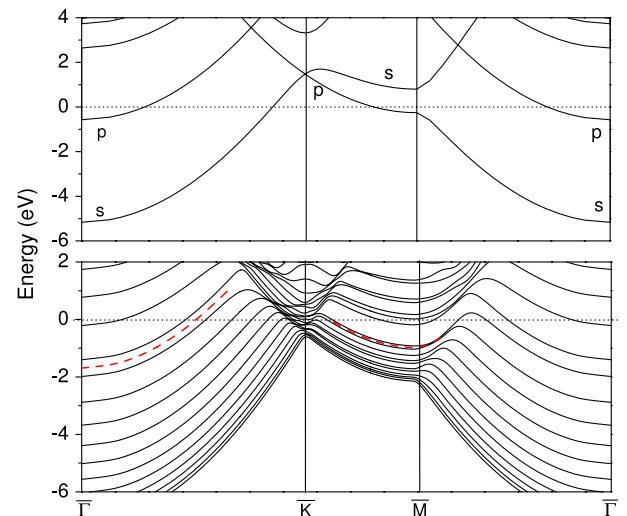


Fig. 1. Top panel shows the computed electron band structure of a Mg monolayer. In the bottom panel electronic structure of the Mg(0001) surface is presented. Dashed lines indicate surface states at $\bar{\Gamma}$ and \bar{M} .

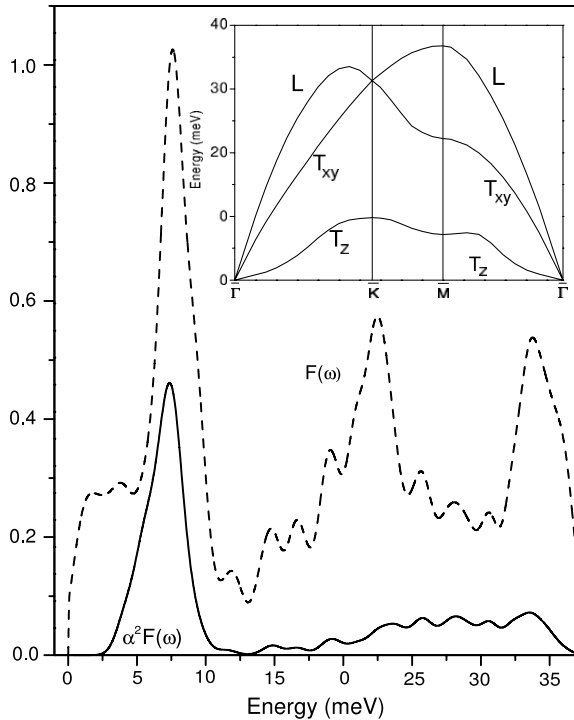


Fig. 2. Dashed and solid lines show, respectively, the density of phonon states, $F(\omega)$, and the Eliashberg function, $\alpha^2 F(\omega)$, averaged over the Fermi surface, see Eq. (3), for the Mg monolayer. In the inset the phonon dispersion curves are presented.

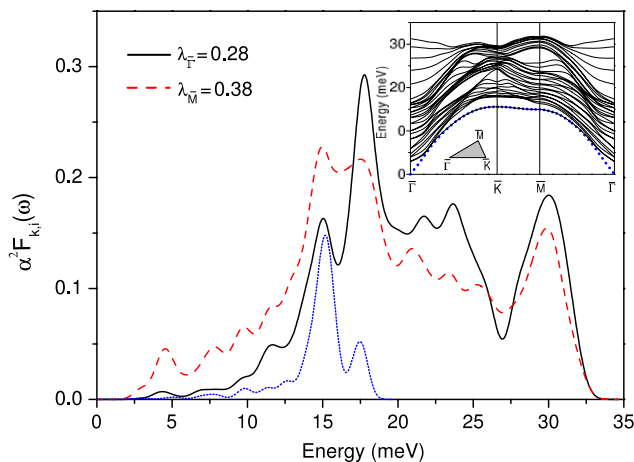


Fig. 3. The solid line represents the Eliashberg function of the surface state at the \bar{T} point. The dashed line indicate the surface state at \bar{M} . The dotted line shows the Rayleigh mode contribution to the Eliashberg function of the surface state at \bar{T} . The inset panel is for the phonon dispersion.

spectral function $\alpha^2 F(\omega)$ averaged over states at the Fermi surface. Electrons which are being scattered from one part of the Fermi surface to another, interact mostly with phonons of energy 6–8 meV. These phonons correspond to the previously mentioned perpendicular vibrations and are the most efficient modes in the coupling. At higher energies, although the presence of phonons is guaranteed as it can

be seen in the figure, matrix elements of the coupling lower the contribution to the coupling of these modes.

For the 11-layer slab, calculated phonons form 33 branches as shown in the inset of Fig. 3. The surface Rayleigh mode is drawn in blue, and represents the perpendicular vibrations of atoms of the outermost layer of the slab. This time, the Eliashberg functions depicted are not averaged over electron states, they represent selected initial electron states that interact with phonons of any energy as defined in Eq. 2. More precisely, we have chosen as initial electron states, surface states at \bar{T} and \bar{M} points. At around 15 meV there is a pronounced peak in the Eliashberg spectral function of the \bar{T} surface state. This is due to the coupling of this electron state with the Rayleigh mode. Somehow this is an expected feature of the spectrum since the electron surface state at this point has a sp_z polarization[16], which is in the same polarization of the phonon mode. This large overlap between electron wavefunction and the direction of the phonon mode turns into a big value of the matrix element. Surface state at the \bar{M} point is a different case because its polarization is of the form p_x, p_y [16] and hence the overlap with the Rayleigh mode should not be so strong, however, the peak is still observed at 15 meV. This is due to the fact that there exists a high concentration of phonons with such energy and short wave vectors that enable electronic interband transitions around the \bar{M} point.

Finally, we compute the electron–phonon coupling parameter λ for both surface states. We find $\lambda_{\bar{T}} = 0.28$ for the \bar{T} surface state and $\lambda_{\bar{M}} = 0.38$ for the \bar{M} surface state. Kim et al. [17] have experimentally measured the λ value for the \bar{T} surface state by measuring its linewidth at different temperatures in angle resolved photoemission experiment. They have obtained a value of 0.27(2), which is in good agreement with our result.

Acknowledgements

This work was partially supported by the University of the Basque Country, the Departamento de Educación del Gobierno Vasco, and MCyT (Grant No. FIS 2004-06490-C03-01).

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