

Li atoms deposited on single crystalline MgO(001) surface. A combined experimental and theoretical study

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Abstract

In this Letter the interaction of Li atoms with terrace sites of MgO(001) surfaces is characterized by combining EPR spectroscopy with theoretical calculations. The Li atoms adsorbed to MgO terrace sites show a reduction of the isotropic hyperfine coupling constant by approximately 50% with respect to Li atoms in the gas phase. In combination with theoretical calculations it can be shown that this reduction of the hyperfine coupling constant is not due to a charge transfer between Li and MgO but can be understood by a polarization of the Li atoms which are essentially neutral.

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1. Introduction

Oxide surfaces play an important role in a variety of technological applications. In particular the functionalization of oxide surfaces is of particular importance in this respect. This may be achieved by depositing additional material such as metal particles on their surface as it is often found for heterogeneous catalysts [1]. Another approach is to change the electronic properties of the surface e.g. by creating electron rich surface sites [2]. To this end alkali metals are often used and MgO with its simple electronic and geometric structure is an ideal model surface [3–6]. EPR spectroscopy has proven to be well suited to characterize the interaction between paramagnetic alkali metal atoms and ionic oxides and it has been proposed that the EPR properties measured for such systems provide a measure of the oxide basicity [7]. The interaction of lithium with MgO is one of the classical examples which trans-

forms MgO into a catalyst capable for methane activation presumably by the creation of electron deficient oxygen centers [8]. In order to understand such complex processes on a molecular level it has been proven a valuable approach to study model systems which retain the essential ingredients of the complex system, however, offering a characterization with the rigor of modern surface science technology [9,10]. The aim of the present Letter is to characterize the simplest system for the interaction of Li with a MgO surface namely Li atoms adsorbed on terrace sites of a MgO(100) surface. To the best of our knowledge, while EPR experiments on the properties of adsorbed Na, K, and heavier alkali atoms have been reported [5], this is the first report on the properties of Li atoms.

2. Experimental and theoretical details

For the EPR experiments, Li atoms were deposited at 35 K on a 20 monolayer (ML) thick MgO(001) film grown on a Mo(001) substrate. The Li atoms were evaporated from an SAES-getter and the deposited amount is given as the hypothetical thickness of a continuous metal film

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which was measured by a quartz microbalance. The Mo substrate was cleaned by oxidation with O_2 at 1500 K and subsequent flashes to 2300 K. MgO films were prepared by reactive deposition of Mg in an oxygen background pressure of 1×10^{-6} mbar at a substrate temperature of 600 K and a deposition rate of 1 ML MgO/min. In order to improve the size of the terraces, the MgO film was annealed to 1100 K for 10 min. The EPR spectra of Li atoms were measured at 30 K using a Bruker EMX X-Band spectrometer operating at approximately 9.65 GHz. For the current spectra a microwave power of 2 mW and a modulation amplitude of 4 G were used. Details of the experimental setup are described elsewhere [11]. The simulations of the EPR spectra were done using the EasySpin package [12].

The EPR properties have also been determined by DFT model calculations using a cluster approach. The surface of MgO is represented by a finite $Mg_9O_9Mg_{16}^*$ nano-cluster. The central part, Mg_9O_9 , is treated quantum-mechanically (QM), and is surrounded by a region of about 1200 classical ions whose polarizability is described by a shell-model (SM) [13]. Cations in the SM region at the interface with the QM region are replaced by ions (hereafter indicated as Mg^*) on which an effective pseudopotential (ECP) is centered to avoid non-physical polarization of QM interface anions. Region I, QM and SM, is then surrounded by a large array of point charges (3200 PC) in order to reproduce the long-range electrostatic potential. This scheme is implemented in the GUESS code [14] interfaced with the GAUSSIAN 03 code [15]. All centers in the QM region and Mg^* interface atoms have been allowed to move during the geometry optimization, while only shells, not cores, have been relaxed in the SM region. Thus, the electronic polarization has been included in a large portion of the surface, while ionic polarization is restricted to a few tens of atoms.

The total energy and the electronic structure of the QM cluster are calculated using the hybrid B3LYP exchange-correlation functional [16,17]. For the EPR properties of the Li adatom we have considered the hyperfine coupling constants (both isotropic and dipolar parts), and the g -factors. For the calculation of the g -factor we used the spin-orbit perturbation strategy in the scheme proposed by Neese [18], and implemented in GAUSSIAN 03. The 6-31+ G^* and 6-311+ G^* basis sets has been used for Li, while the atoms of the MgO cluster were treated with a standard 6-31G basis set, except for the central adsorbing O atom treated with the 6-31 G^* basis set.

3. Results and discussion

Fig. 1a shows the EPR spectrum after deposition of nominally 0.15 Å Li at 35 K on a 20 ML thick MgO(100)/Mo(100). The spectrum was measured with the magnetic field oriented parallel to the surface and exhibits a quartet of lines. This quartet is characteristic for Li atoms which are adsorbed on the MgO(100) surface. Comparing the signal intensity of the EPR signal with the intensity observed for the same nominal amount of Au the

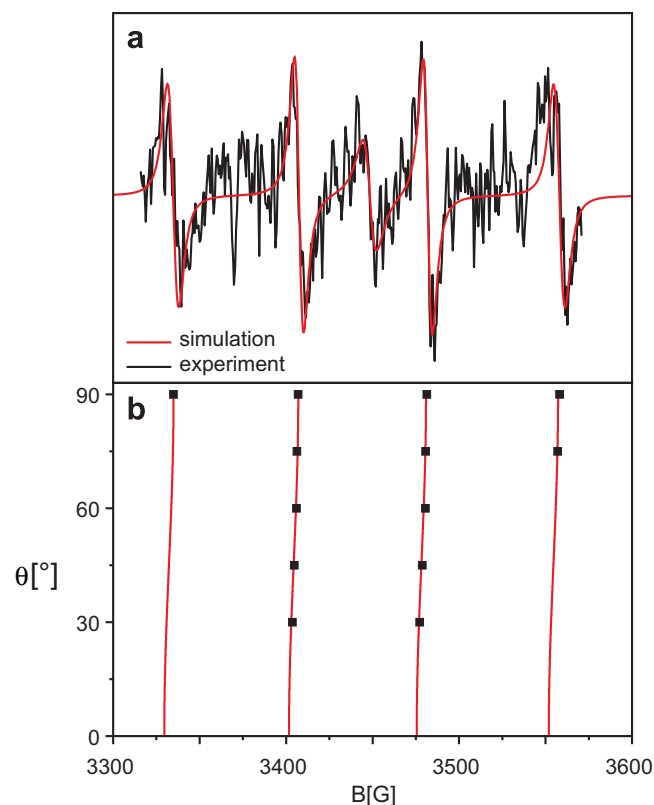


Fig. 1. (a) EPR spectrum (black trace) of 0.15 Å Li deposited at 35 K on a 20 ML thick MgO(100) film on Mo(100). The magnetic field is oriented in the surface plane. A simulation of the spectrum assuming Li atoms (quartet of lines) is shown in red. The signal in the center is added to the simulation as a second component. (b) angular dependencies of the resonance positions. The angle θ is defined the angle between the surface normal and the static magnetic field. Red traces are simulation; for details see text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

signal of the Li atoms is smaller by about a factor of 3 which indicates that the Li atoms observed by EPR are most likely not the majority species on the surface [19]. In addition, the spectrum exhibits a smaller signal close to the isotropic g -value which gains intensity for increasing amount of Li. Similar signals have already been observed for alkali metal deposition on powders [4], but a detailed discussion of this signal is beyond the scope of the present letter and will be discussed elsewhere. Fig. 1b shows the resonance positions of the four signals attributed to Li atoms shown in Fig. 1a as a function of the angle between static magnetic field and surface normal. From a fit to the angular dependent signals it is possible to deduce not only the g - and A -tensor components, but also their orientation with respect to the surface. This analysis was performed using the EasySpin package [12] and the result is collected in Table 1. As compared to the gas-phase, the g_{\perp} -value in the surface plane is reduced while the g_{\parallel} -value describing the normal component is slightly increased (see Table 1). From the angular dependence of the resonance positions it is possible to deduce the orientation of the tensor which has to be chosen with the parallel component aligned to the

Table 1
Experimental and theoretical g- and A-coupling matrix elements for ${}^7\text{Li}$ atoms on MgO(100) terrace sites

| | Basis set | Li | Li/MgO(100) | | | | |
|------------|-----------|----------------------|-------------------|-------------------|---------------------|-----------------|-----------------------------------|
| | | a_{iso} [G] | g_{\parallel} | g_{\perp} | B_{\parallel} [G] | B_{\perp} [G] | a_{iso} [G] ^a |
| Experiment | – | 143.4 | 2.003 ± 0.001 | 2.000 ± 0.001 | 0 | 0 | 74 ± 0.5 (51.6%) |
| Theory | 6-311+G* | 155.5 | 2.0022 | 2.0011 | 0.7 | –0.3 | 75.5 (48.5%) |
| | 6-31+G* | 129.4 | 2.0022 | 2.0012 | 0.6 | –0.3 | 73.5 (56.8%) |

^a Percentage in parenthesis is given with respect to the free atom.

surface normal. Due to the fact that the orientation of the tensor has to reflect the local symmetry of the adsorption site, the measured angular dependence provides experimental evidence for the observed Li atoms to be adsorbed on terrace sites of the MgO surface. The hyperfine coupling constant was found to be isotropic within the accuracy of the experiments. With respect to the gas phase a significant reduction of the isotropic hyperfine coupling constant from 143.2 G (401.7 MHz, $g = 2.00231$) [20] to 74 G is found. What is the reason for this reduction of the isotropic hyperfine coupling constant which reflects the spin density at the nucleus? A possible explanation would be a charge transfer from or to the Li atom which would correspond to a transfer of spin density onto the MgO substrate. Recent combined experimental and theoretical efforts have shown that it is also possible to explain such a reduction of the isotropic hyperfine coupling constant by a polarization of the spin density away from the surface resulting in essentially neutral K or Au atoms [4,19]. To discriminate between these cases the experimental parameters are compared to calculations of Li atoms adsorbed on terrace sites of the MgO surface.

The calculations show that, as for other alkali metals, the preferred adsorption sites on the MgO surface are the oxygen anions. As seen from Table 1, the isotropic hyperfine constant is calculated to be 75.5 G with the 6-311+G* basis set, which is in good agreement with the measured value of 74 G. Since the computed value for the free atom using the same basis is 155.5 G (12 G larger than in the experiment), this corresponds to a reduction of about 50% with respect to the gas phase. The 6-31+G* basis set gives similar results: the a_{iso} for the free Li atom is 129.4 G (14 G smaller than in the experiment) while on the surface the value is 73.5 G, more or less the same value obtained experimentally or with the more flexible 6-311+G* basis set. In addition, it is worth noting that theory does predict a very small dipolar contribution to the hyperfine coupling constants which is perfectly in line with the experimental results. The calculated g-values show the same qualitative trend of a larger g-value for the normal as compared to the in-plane orientation as the experimental results. However, the quantitative discrepancies are within 0.1% which is well in line with previous experience for g-values calculated for paramagnetic color centers e.g. [21]. A closer evaluation of the calculation reveals that the reduction of the isotropic hyperfine coupling constant is related to a polarization of the spin density away from

the surface as shown in Fig. 2. This is the same mechanism previously found for Au atoms on MgO terrace sites [19] or for K atoms on more complex morphological sites such as reverse corners [5]. The polarization is driven by the Pauli repulsion between the rather diffuse unpaired electron of the Li atom and the valence electrons of the oxygen ions of the MgO surface. As compared to the other alkali metals this effect is rather strong for Li, because of the relatively short distance – calculated to be 1.83 Å – between the Li atoms and the MgO surface which is a consequence of the rather large binding energy ($D_{\text{e}}(\text{calc}) = 1.05$ eV; without BSSE correction) for MgO terrace sites. For the heavier alkali metals the bonding becomes weaker and conversely the calculated reduction of the isotropic hyperfine coupling constant (as compared to the gas phase) is significantly smaller resulting in a reduction of only about 38% and 23% for Na and K, respectively [5,6].

However, the rather large binding energy of the Li atoms does not imply that a diffusion of the atoms on the surface is difficult, too. Annealing experiments to slightly higher temperatures reveal that the Li atoms on

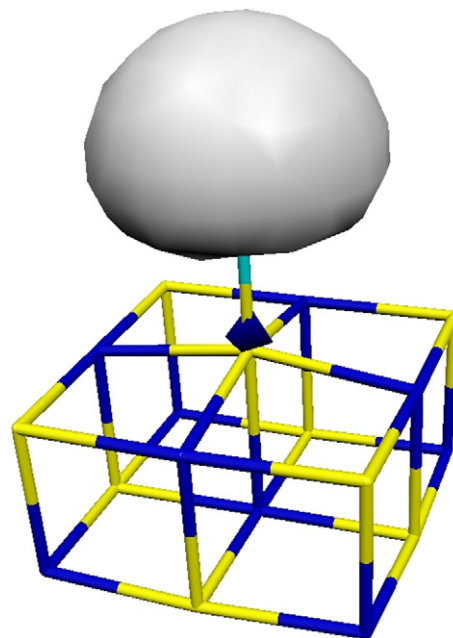


Fig. 2. Plot of the unpaired electron wave function. The QM cluster is represented by the stick model with O atoms in yellow and Mg atoms in blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

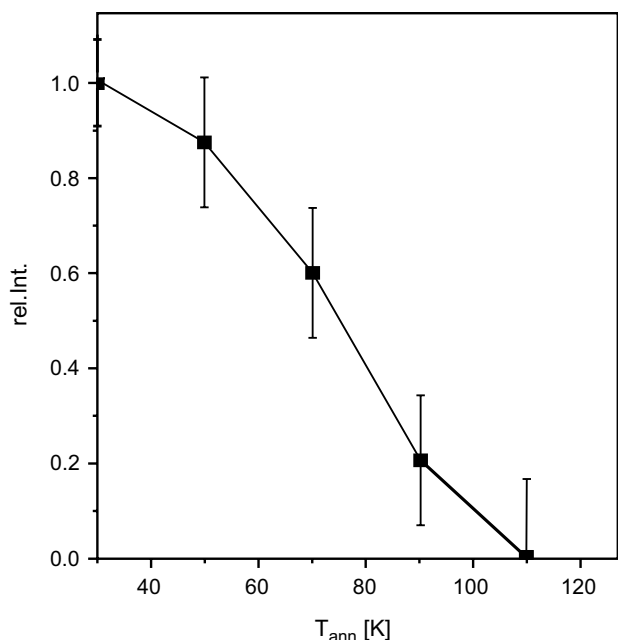


Fig. 3. Relative intensity of the EPR signal of 0.15 \AA Li deposited at 35 K onto a 20 ML thick MgO(100) film on Mo(100) with respect to the annealing temperature.

the MgO(100) terrace start to diffuse on the surface above about 50 K. This can be monitored by a decrease of the EPR signal intensity. In Fig. 3 the EPR intensity is plotted as a function of the annealing temperature showing that the intensity is lost above 110 K. Assuming a simple activated diffusion with a typical exponential prefactor of about 5×10^{12} this corresponds to an activation barrier of approximately 0.17 eV. The system behaves rather similar to Au atoms adsorbed on the same surface. The adhesion energy of Au atoms is about the same as those for Li and was calculated by several groups to be around or slightly below 1 eV [22–26]. In addition, the diffusion energy was calculated to be around 0.2 eV. This fits nicely with the onset of translational dynamics for Au atoms which found to be around 80 K on the MgO(100) surface [27].

In summary it was shown that a combination of EPR spectroscopy and theoretical calculations allows for a detailed characterization of Li atoms adsorbed to terrace sites MgO(100) surfaces. From an analysis of the isotropic hyperfine coupling constant it is inferred that the reduction of this quantity is due to a polarization of the Li atoms which remains essentially neutral. The polarization effect

is rather strong for Li atoms on the MgO terraces due to the relatively strong binding to the surface.

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