Induced resistivity of magnetic impurities in the proximity of a metal surface

M. I. Trioni,[1] H. Ishida,[2] and G. P. Brivio[1,3]

[1]*Istituto Nazionale per la Fisica della Materia, UdR Milano Bicocca, via Cozzi 53, 20125 Milano, Italy*
[2]*College of Humanities and Sciences, Nihon University, Sakura-josui, Tokyo 156, Japan*
[3]*Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, via Cozzi 53, 20125 Milano, Italy*
(Received 7 August 2001; revised manuscript received 26 November 2001; published 13 March 2002)

The induced surface resistivity ρ_s of $3d$ adatoms is calculated on a semi-infinite Al-like jellium within the density-functional theory in the local-spin-density approximation (LSDA). The unexpected nonmonotonic behavior of ρ_s, as function of the position of the atoms with respect to the surface, recently found for most of $3d$ adatoms in calculations without spin polarization in the local-density approximation (LDA), is confirmed. However, the intensity and the dependence on the atomic number of ρ_s is modified by the LSDA in a significant way. At the equilibrium adsorption site on clean Al, the largest resistivity is found for Fe, not for Cr, which is different from the LDA results. The relationship between the maxima of ρ_s, the magnetic moment and the density of states induced by the adatom on the surface is discussed.

I. INTRODUCTION

The resistivity induced by adatoms and molecules on thin metal films is a very important phenomenon for several reasons. Its strong sensitivity to the surface geometry and topology, such as roughness, steps, and defects in general, makes it a valuable tool for monitoring the growth conditions of a thin metallic film.[1] Advances in nano manipulation techniques allow for a detailed analysis of the previous effects on the atomic scale. A simple equation for the adsorbate-induced resistivity ρ_s derived by Persson, also shows that ρ_s is directly related to the electronic friction and the damping of the infrared parallel vibrational modes of the adsorbed molecules.[2] Regarding the latter property there are recent experimental works in which the infrared reflectance and the dc resistance changes were measured during adsorption of molecules on copper.[3,4]

Theoretical studies of surface resistivity are still scarce. Only recently a general expression of the induced surface resistivity beyond the spherical symmetry has been worked out.[5] *Ab initio* calculations of surface resistivity due to adatoms in this framework have only been performed on a semi-infinite jellium.[6,7] In fact, although adsorbate overlayers on a thin, clean metal slab are expected to increase the experimental film resistivity, such an effect cannot be computed in the standard slab approach that assumes a supercell geometry for the overlayer structure. This is because in such calculations a perfect two-dimensional periodicity does not allow for infinitesimal electron-hole pair excitations, which are the essential processes in resistivity.

The study of the electronic properties of a metal surface covered with an overlayer of magnetic adatoms is also an important topic in surface physics, as it is related to several fundamental as well as applied issues from the magnetism of dilute alloys to the efficient storage of data. In a previous paper,[7] to be referred to as I hereon, we computed the surface-induced resistivity of $3d$ adatoms on semi-infinite Al jellium within the density-functional theory (DFT) framework in the local-density approximation (LDA), without explicitly considering the spin polarization of the electrons. As

a first step such a calculation was useful to know the trends of the induced resistivity of those impurities, which showed an unexpected behavior with a maximum for some $3d$ atoms at a certain position from the surface. However, one should realize that most of $3d$ adatoms can display a magnetic moment even on the electronically densest metals such as Al, since they experience a reduced charge density compared to bulk. So one expects this property to affect the previously mentioned nonmonotonic behavior of the induced resistivity. For this reason, in this paper we extend the LDA results by carrying out a spin-polarized calculation within the local-spin-density approximation (LSDA) of the DFT. We shall use the embedding method for the isolated adsorbate, which treats a single particle interacting with a semi-infinite solid.[8-10] This approach is most suitable for dealing with a very dilute overlayer. Since it is able to consider the continuous eigenenergy spectrum of a semi-infinite metal, it can accurately account for the adatom-induced resonances whose properties at the Fermi level are central to the understanding of the induced resistivity.[2,7] In our approach the semi-infinite solid is described by Al-like jellium. Such a model accounts for the substrate of the adsorption system in a simpler way, and consequently is amenable to calculating the adatom induced resistivities, at any atom position normal to the surface, say, z_a. This allows one to understand in detail how the impurity-induced resistivity changes from its asymptotic bulk value to that characteristic of an adsorbate. From our LSDA calculations, we establish a new dependence of the adatom resistivity both on z_a and on the atomic number Z, and we shall analyze features absent in our previous LDA calculation in detail.

In the following section, we present and discuss all the results, while the last one is devoted to the conclusions.

II. RESULTS

Since all details of the embedding approach[8,9] and of the resistivity calculation[6,7] have already been discussed, in this paper we only report the equation of the adatom-induced residual resistivity for a spin-polarized system
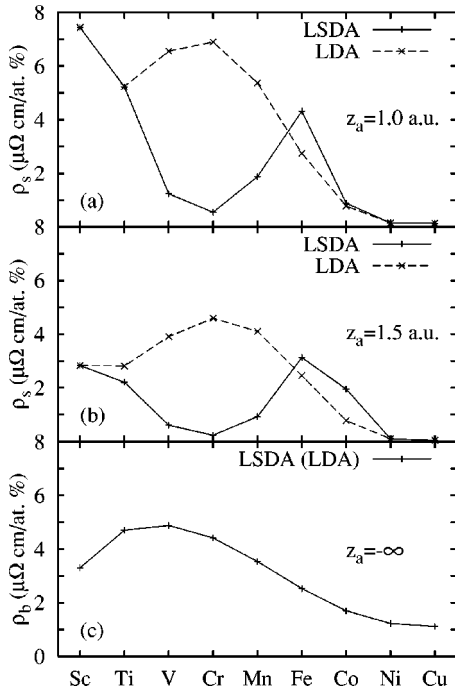
FIG. 1. Resistivity induced by $3d$ adatoms on Al at atom-surface position $z_a = 1$ a.u. (a), $z_a = 1.5$ a.u. (b), and as interstitial impurity (c), by the LSDA (solid line) and the LDA (dashed line).

$$\rho_s = \frac{\hbar}{V \pi n_e^2 e^2} \sum_\sigma \int d\mathbf{r} \, d\mathbf{r}' \, \mathrm{Im}\, G^\sigma(\mathbf{r}, \mathbf{r}', E_F)$$

$$\times \frac{\partial V_{\mathrm{eff}}^\sigma}{\partial x'} \mathrm{Im}\, G^\sigma(\mathbf{r}', \mathbf{r}, E_F) \frac{\partial V_{\mathrm{eff}}^\sigma}{\partial x}. \tag{1}$$

In Eq. (1) $G^\sigma(\mathbf{r}, \mathbf{r}')$ is the spin (σ)-dependent Green's function solution of the Kohn-Sham equation and $V_{\mathrm{eff}}^\sigma(\mathbf{r})$ its effective potential in the LSDA; V, n_e, and E_F being the volume per adatom, the conduction electron density in the substrate, and the Fermi energy, respectively. Because of the cylindrical symmetry of the system about a z axis pointing towards the vacuum from the jellium edge and passing though the adatom, derivatives can be taken in any direction normal to $\hat{z}$.

In Fig. 1, we report the surface resistivity induced by $3d$ atoms on Al as function of the atomic number Z, at two atomic positions from the jellium edge, namely, $z_a = 1$ a.u. [Fig. 1(a)] and $z_a = 1.5$ a.u. [Fig. 1(b)], where the dashed and solid lines refer to values obtained with the LDA and the LSDA, respectively. The magnetic moments of these adsorbates calculated within the LSDA framework are listed in Table I (a detailed discussion about this magnetic behavior is

TABLE I. Magnetic moments (μ_B) of $3d$ adatoms on Al at two different distances from the surface.

z_a (a.u.)	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
1.0	0.0	0.0	3.2	3.9	3.4	2.2	0.3	0.0	0.0
1.5	0.0	1.9	3.5	4.4	3.9	2.7	1.2	0.0	0.0

reported elsewhere[11]). We note that when the adatoms have a finite magnetic moment, the calculated induced resistivities by the LSDA become very different from the corresponding LDA ones, which display a bell-shaped curve of ρ_s, as function of Z. In particular, it is observed that the minimum in the LSDA resistivity curve corresponds instead to a maximum in the LDA results. For comparison, in Fig. 1(c) we also show the resistivities induced by the *interstitial* bulk impurities, which have been computed by placing the $3d$ atoms at $z_a = -\infty$ inside jellium. In this configuration the magnetic moment of all these impurities disappears because of the high density of the substrate and the LSDA results coincide with the LDA ones. To describe bulk impurities, it may be more realistic to consider *substitutional* ones. Within the jellium model this can be done by taking away a sphere of positive-charge background containing exactly the valence electrons of the substituted atom of the host. However, in this paper we also deal with $3d$ atoms inside jellium but very close to its edge. In such a case the impurity nucleus may be surrounded by only a portion of the above-mentioned sphere-of-charge background. So we prefer describing such a system for $z_a < 0$ by an *interstitial* impurity. Regarding the *substitutional* impurities, previous theoretical works[12–14] report that Cr, Mn, and Fe may possess a magnetic moment in bulk Al depending on the detailed features of each calculation. Experimental data suggest that $3d$ impurities are nonmagnetic in Al with the possible exception of Cr and Mn, for which spin fluctuations manifest themselves in dependence of the residual resistivity on the temperature.[15]

On the contrary, when some of $3d$ bulk impurities are magnetic, like in metals with lower electronic densities such as Cu and Ag, the $3d$ impurity resistivity,[16] as function of Z, deviates largely from the bell-shaped behavior and resembles ρ_s (solid line) in Fig. 1(a) and 1(b): The resistivity curve exhibits a minimum at Cr and a maximum at Fe. This suggests that the behavior of ρ_s, as function of Z, is mainly related to the magnitude of the local charge density at the impurity site vis à vis the existence of a magnetic moment. In fact we have verified that at distances from the surface such as those in Figs. 1(a) and 1(b), the Al-jellium-tail charge densities are close to the average electronic charge densities in the vacancy region of a *substitutional* impurity in bulk noble metals. Also note that the magnetic moments in Table I resemble those in Cu (first row) and Ag (second row) bulks.[16]

Figure 2 shows the adatom-induced resistivity, calculated in the LSDA, as function of both Z and z_a, varying from $z_a = -3$ to $z_a = 3$ a.u., or in other words, from the asymptotic value of the bulk impurity to that of an atom far from the surface. As previously discussed, our results merge to the bulk *interstitial* impurity values shown in Fig. 1(c). Furthermore, from a comparison with a recently performed total-energy calculation of $3d$ adatoms on a periodic Al(100) surface by using the slab model,[11] we infer that the adatom equilibrium position on the real substrate corresponds to the one on jellium, which lies between $z_a = 1$ a.u. and $z_a = 1.5$ a.u. from its edge for all $3d$ atoms.

In Fig. 2, we observe that the induced resistivities display a behavior as function of z_a strongly dependent on Z. In
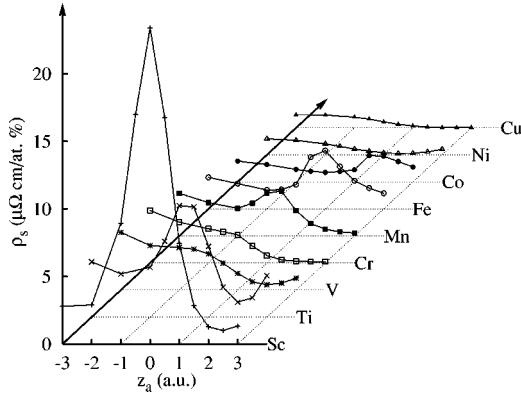
FIG. 2. Resistivity induced by $3d$ adatoms as function of the distance z_a from the Al surface.

particular, we note that the impurity-induced resistivities of Sc, Ti, Mn, Fe, and Co vary from the asymptotic *interstitial* impurity value, say ρ_b, and show a maximum, which is larger or comparable to ρ_b and whose position varies depending on Z. We have verified that the enhancement of the adatom-induced resistivity at the maximum with respect to the calculated bulk *substitutional* impurity-value[13] occurs only for Sc, Ti, and Fe, and solely for the last atom such a maximum lies at about the equilibrium adsorption position. Note that the largest value of ρ_s in Fig. 2 is attained by Sc when located at the jellium edge. But ρ_s of Sc diminishes rapidly both by decreasing and increasing z_a. Since up to our knowledge there are no previous results for the impurity induced resistivity of Sc in the proximity of the surface, such anomalous behavior cannot be compared with others.

We study now the existence of maxima of ρ_s as function of z_a for all $3d$ adatoms other than Sc, and recall first that maxima of ρ_s as function of z_a were also obtained with a LDA calculation for $3d$ adatoms up to Fe. However, we point out that the LSDA approach modifies the intensity, position, and dependence on Z of the LDA maxima in a significant way. In fact around the equilibrium position, the largest ρ_s is attained by Cr in the LDA (see paper I) while by Fe in the LSDA. So we discuss the dependence of ρ_s on the position from the surface for these two adatoms, namely Fe and Cr, for which the difference between the LDA and LSDA results is most striking. These functions are shown in Figs. 3(a) and 3(b) for Cr and Fe, respectively, from $z_a = -3$ to $z_a = 3$ a.u. In the LSDA calculations, while ρ_s of Cr shows a slow monotonic decrease from ρ_b by varying z_a, that of Fe displays a more complex behavior with a fairly shallow maximum around $z_a = 1$ a.u. Therefore, very accurate measurements of the induced resistivity should be rather insensitive to the position of a Cr adatom in the proximity of the surface. Instead they could help understanding whether a Fe atom is adsorbed just underneath the surface, tucked in it, or adsorbed on kinks, terraces or steps.

In paper I, we have demonstrated that the magnitude of ρ_s mainly depends on that of the induced density of states (IDOS) at the Fermi energy E_F. This result is confirmed by the LSDA analysis. In Fig. 4, we plot the spin dependent IDOS's, $n^\sigma(\epsilon)$, for Cr and Fe at $z_a = 1$ a.u. defined by
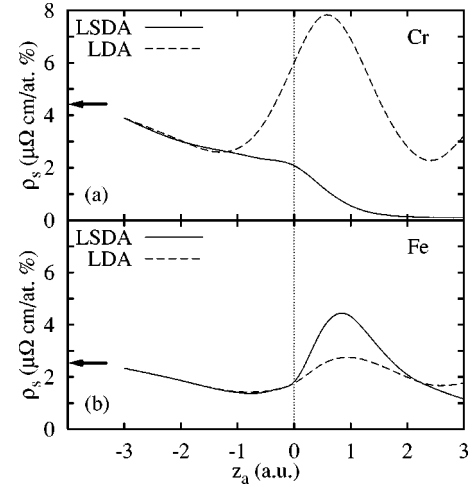

FIG. 3. Resistivity induced by Cr (a) and Fe (b) as function of the distance z_a from the Al surface, by the LSDA (solid line) and the LDA (dashed line). The arrows on the left refer to the resistivity for the same (interstitial) atom in Al bulk.

$$n^\sigma(\epsilon) = \frac{1}{\pi} \int d\mathbf{r}\, \mathrm{Im}[G^\sigma(\mathbf{r},\mathbf{r},\epsilon+i\delta) - G_0^\sigma(\mathbf{r},\mathbf{r},\epsilon+i\delta)],$$

$$(2)$$

where G_0 denotes the Green's function of the clean substrate. As expected, in the LSDA approach the majority- and minority-spin populations split up and two maxima appear in the IDOS with a minimum in between them. Depending on the relative position of the Fermi level with respect to such extrema, the values of ρ_s, roughly proportional to the IDOS at E_F, may be very different. For Cr, the magnitude of the IDOS at E_F is about its minimum, hence ρ_s is indeed very small. For Fe, on the contrary, the minority-spin population displays a maximum exactly at E_F, which clearly accounts for the largest ρ_s. On examining Fig. 3 we see that the increase in ρ_s for Cr at $z_a \geqslant 3$ a.u. in the LDA calculation is
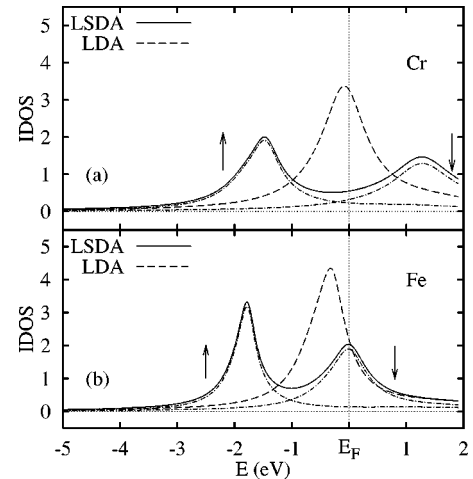

FIG. 4. Induced density of states (states/eV) of Cr (a) and Fe (b) at $z_a = 1$ a.u. on Al, by the LSDA (solid line) and the LDA (dashed line). $\uparrow$, majority-spin population, $\downarrow$, minority-spin population (dash-dotted line).

not confirmed by the LSDA calculation. For this latter approach such a nonphysical behavior starts at $z_a > 4$ a.u. This is expected, since the LSDA, though not accounting for correlation of two separate subsystems correctly, is a much better approximation for such a magnetic atom than the LDA. In this case, since for atoms farther away from the surface and open-shell systems, it pins only electrons of one spin population, the divergent behavior already discussed[7] starts at larger atom-surface distances.

III. CONCLUSIONS

In this paper, we have presented a full calculation of $3d$ atom-induced resistivities in the proximity of a metal (Al-like jellium) by the LSDA. Our results demonstrate that the LSDA approach is a necessary tool to describe ρ_s, since the induced resistivities are significantly different from those calculated in the LDA in paper I. We observe that for some $3d$ atoms ρ_s displays a nonmonotonic behavior by varying the atom position normally to the surface. This property, which is sensitive to the local charge density sampled by the adatom, could help in determining the impurity local chemisorption environment. Only for Fe the maximum of ρ_s occurs when this adatom is about its equilibrium position on a clean, flat Al surface. We have investigated the relationship between ρ_s and the magnetic moment of $3d$ adatoms on Al, and found similarities between our surface results and those of the same impurities in metal bulk of lower electronic density than Al.

The surface-induced resistivity can also be related to the electron-hole pair nanofriction mechanism, though in this case we expect lateral barriers to hamper effective diffusion of $3d$ adatoms. Finally, note that there is no simple way to relate the adatom magnetic moment to the surface-induced resistivity, since the former mainly depends on the difference of spin populations in the ground state, which encompasses the full density of states, while the latter on the density of states at the Fermi level. This dependence could make the adatom-induced surface resistivity a very sensitive tool of the density of states of the adsorbate system at the Fermi level.

[1] D. Schumacher, *Surface Scattering Experiments with Conduction Electrons*, Springer Tracts in Modern Physics Vol. 128 (Springer, Berlin, 1993).

[2] B. N. J. Persson, Phys. Rev. B **44**, 3277 (1991).

[3] M. Hein, P. Dumas, A. Otto, and G. P. Williams, Surf. Sci. **419**, 308 (1999).

[4] C.-L. Hsu, E. F. McCullen, and R. G. Tobin, Chem. Phys. Lett. **316**, 336 (2000); R. G. Tobin, Surf. Sci. (to be published).

[5] H. Ishida, Phys. Rev. B **52**, 10 819 (1995).

[6] H. Ishida, Phys. Rev. B **54**, 10 905 (1996).

[7] M. I. Trioni, H. Ishida, and G. P. Brivio, Phys. Rev. B **63**, 075408 (2001).

[8] M. I. Trioni, G. P. Brivio, S. Crampin, and J. E. Inglesfield, Phys. Rev. B **53**, 8052 (1996).

[9] M. I. Trioni, S. Marcotulio, G. Santoro, V. Bortolani, G. Palumbo, and G. P. Brivio, Phys. Rev. B **58**, 11 043 (1998).

[10] G. P. Brivio and M. I. Trioni, Rev. Mod. Phys. **71**, 231 (1999).

[11] M. I. Trioni, Q. Sun, G. P. Brivio, Z. Yang, and R. Wu, Phys. Rev. B **65**, 104108 (2002).

[12] E. Mrosan and G. Lehman, Phys. Status Solidi B **78**, 159 (1976).

[13] R. M. Nieminen and M. Puska, J. Phys. F: Met. Phys. **10**, L123 (1980).

[14] J. Deutz, P. H. Dederichs, and R. Zeller, J. Phys. F: Met. Phys. **11**, 1787 (1981).

[15] G. Grüner, Adv. Phys. **23**, 941 (1974).

[16] R. Podloucky, R. Zeller, and P. H. Dederichs, Phys. Rev. B **22**, 5777 (1980).