

# Adsorbed 3d transition metal atoms and clusters on Au(111): Signatures derived from one-electron calculations.

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## Abstract

The spectroscopic characteristics of systems with adsorbed  $d$  impurities on noble metal surfaces should depend on the number and geometric arrangement of the adsorbed atoms and also on their  $d$  band filling. Recent experiments using scanning tunneling microscopy have probed the electronic structure of all 3d transition metal impurities and also of Co dimers adsorbed on Au(111), providing a rich variety of results. In this contribution we correlate those experimental results with ab-initio calculations and try to establish necessary conditions for observing a Kondo resonance when using the single impurity Anderson model. We find that the relevant orbitals at the STM tip position, when it is on top of an impurity, are the  $d$  orbitals with  $m = 0$  and that the energy of these levels with respect to the Fermi energy determines the possibility of observing a spectroscopic feature due to the impurity.

73.20.Hb, 73.40.Gk

The electronic structure of  $3d$  transition-metal impurities on the (111) surface of copper and gold has been studied recently with scanning tunneling microscopy<sup>1-4</sup>. The first measurements, performed only for Co impurities, gave rise to a direct spectroscopic observation of the Kondo resonance for an isolated impurity<sup>1</sup>. Further experiments with Co dimers<sup>2</sup> and with other  $3d$  transition metal atoms<sup>3</sup> show that there is a different behavior of  $dI/dV$  for different impurity  $d$  filling, thus varying significantly across the  $3d$  series in the periodic table. These results provide a rich phenomenology that we believe can be correlated with results of LSDA calculations.

In a previous paper<sup>5</sup> we calculated the electronic densities of states of a periodic system that simulates the experimental situation described above. It consisted of repeated slabs of five layers of Au(111) with Co atoms deposited on both sides of them forming a dilute adsorbed layer. For this purpose we used the FP-LAPW method and the LSDA approximation with the WIEN97 code<sup>6</sup>. The main result of that paper was that the minority spin contribution to the density of states due to the  $3d$  orbitals of Co with  $m = 0$  is a very narrow band located precisely at  $E_F$ , which could be related to the observed experimental feature.

In the present work we have extended the calculation to other transition metals and also to dimers. The unit cell is the same for all the impurity cases, it has five layers of Au with three atoms in each layer. One impurity atom is located on each side of the slab at one of the hollow sites of the Au(111) slab structure forming a  $\sqrt{3} \times \sqrt{3}$  adsorbed layer. The slabs are separated by enough empty space so as to simulate non interacting surfaces. The distance between impurity atoms on the same plane is  $5 \text{ \AA}$ , and their distance to the surfaces is relaxed so as to minimize the energy.

Magnetism can be quantified in these calculations by giving the magnetic moment inside the muffin tin spheres or the  $d$  band splitting for the different impurities. We show these results in Table I, they agree with previous calculations for similar adsorbed systems<sup>7</sup>. The given splittings are those corresponding to the separation between majority and minority centers of the  $m = 0$  narrow band, that we assume is the more relevant one. Both magnitudes,  $\mu$  and  $E_{up} - E_{dn}$ , are seen to be roughly proportional. In order to simplify the

analysis and to compare with results from model Hamiltonian calculations we have made the working assumption that it is enough to consider just the single  $3d$  level with  $m = 0$  in order to correlate the calculated results with the STM experimental ones. These experiments were performed in a small energy range around the Fermi energy of Au, using a bias voltage of less than 0.1 eV. Our calculations indicate that only the majority band of V and the minority band of Co fall within that range. One would then expect similar experimental results for both impurities, but this is not the case<sup>3</sup>.

Local densities of states at the impurity sites, of  $d$  symmetry and for  $m = 0$  in particular, are shown in Figs. 1 to 6. Also shown in that figure are the charge densities in the vacuum region, plotted along the plane perpendicular to the slab at the impurity site, corresponding to two small energy windows close to  $E_F$ . According to the usual theory of STM spectroscopy<sup>8</sup> the tunneling current is directly related to the charge density at the tip position. We see from Figs. 1 to 6 that the magnitude of this charge density along the normal to the surface is in all cases significantly larger for the energy window that contains the  $3d$  orbital with  $m = 0$  symmetry, namely  $w1$ . The largest hybridization with the conduction electron sea therefore takes place at the energies where the  $m = 0$  symmetry provides the largest contribution. Thus, tunneling conductance should be essentially affected by the presence of these symmetries on the impurity atoms if they happen to fall in the narrow energy window where the experiments are made. This effect should be observed both for minority or majority spins, if the energy conditions were given.

When analyzing each case in more detail we see that for Ti the majority spin electron density in window  $w1$  is about one order of magnitude larger than the minority contribution at the tip site (4 to 5 Å, from the surface) and also larger than the contributions of both majority and minority character in the other window ( $w2$ ). This agrees very well with the observed increase in the STM signal when the bias voltage sweeps energies from below to above the Fermi level, going across this last one. We believe this reflects the increased density of states just above the Fermi level, when electrons start to flow from the tip into the empty states added by the impurity. Because of the experimental width of this feature

it is possibly not a manifestation of the Kondo effect. The second largest value for the ratio of charge density in window  $w1$  versus the one in window  $w2$  is obtained for Ni, and may be interpreted in a similar way as that of Ti, although the magnitudes are much smaller. This system could not show a Kondo effect as it is non-magnetic. For Cr and Fe the relevant states are not close to  $E_f$  so that their influence due to hybridization should not be visible. The cases of Co and V, where we find a narrow band peaked at  $E_f$ , present very similar values of the ratio of charge densities in both windows, being this ratio of the order of 2. Besides this, the absolute charge density values are also very small. We shall analyze below in which cases one could expect a signature of the Kondo peak.

An important one-electron feature, not considered in our calculations, is the interaction of the adsorbed atoms with the (111) surface state at the  $\Gamma$  point of noble metals. This state is responsible for the appearance of standing wave patterns in quantum corrals, and also possibly of recently observed mirages<sup>4</sup>. Our representation of the surface by slabs that are only five layers thick would give a poor approximation of the surface state but the periodicity of the adsorbed atoms, that are not too far away from each other, probably destroys the surface state completely. As a first approximation we assume that this interaction will not depend on  $d$  band filling.

To study the importance of many body effects not considered in the LSDA calculations the single impurity Anderson Hamiltonian (SIAM) is one of the usual approaches<sup>9</sup>. It is known to be equivalent, for most sets of parameters, to the Kondo model Hamiltonian, through the Schrieffer-Wolf transformation<sup>10</sup>. It consists of a conduction band, that provides the Fermi energy or zero energy, and a single magnetic impurity level at  $E_0$ . This level interacts with the band, thus acquiring a width  $\delta$ , and electrons with opposite spins occupying that level feel a Coulomb repulsion  $U$ . The mean field solution of this model Hamiltonian results in two narrow bands, centered at  $E_0$  and  $E_0 + U$ , which could be parametrized for the different adsorbed systems using the results of our LSDA calculations, for example setting for  $E_0$  and  $E_0 + U$   $E_{up}$  and  $E_{dn}$  of Table I, respectively. The many body solution of this model Hamiltonian gives rise to a narrow peak at the Fermi level of the spectral function.

This Kondo peak is always present at  $T=0$ , except when  $E_0$  (or  $E_0 + U$ ) is closer than  $\delta$  to the Fermi energy. In this situation, the mixed valence case, the many body feature is masked inside the broader one-electron peak<sup>11</sup>. The possibility of actually seeing the Kondo peak experimentally is limited by the exponential dependence of the Kondo temperature on the separation of  $E_0$  (or  $E_0 + U$ ) from the Fermi energy. This may be the reason why it is not seen for most of the  $3d$  transition metal impurities. For Co and V the present LSDA calculations give the  $m = 0$  level very close to  $E_F$  and would therefore predict the possibility of observing a Kondo peak in both cases. However, in the case of Co the density of states for  $m = 0$  shows narrower features than for V, this last one spreading more uniformly within an energy range of more than 0.2 eV. This could explain why no special STM feature is observed in V. It is well known that the LDA approximation enhances the width of hybridization peaks, so that we are not able to decide if the observed feature in the case of Co is essentially many body (Kondo) or not. The temperature dependence would of course help to answer this question. In any case, only when one of the two levels, at  $E_0$  or at  $E_0 + U$ , is close to  $E_F$  there is a possibility of observing this narrow feature.

When two Co impurities are brought close together<sup>2</sup> the experimental feature of the single Co impurity disappears. In a simple tight-binding model one would expect a splitting of both the majority and the minority spin levels due to the interaction between the two impurities, giving rise to pairs of bonding and antibonding states. To perform an LSDA calculation similar to the previous one requires a much larger unit cell in order to prevent each dimer from interacting with the others. For this last reason we performed a simplified calculation, using only one monolayer of Au(111) and depositing dimer rows on one side of it. The two atoms in the dimer were placed at a separation of  $2.87\text{\AA}$ , in two next nearest neighbour hollow sites of the surface, and atoms in different dimers were situated at least  $5\text{\AA}$  apart. For Co dimers in the ferromagnetic configuration we found a dimer magnetic moment of  $4\mu_B$  and the  $m = 0$  majority levels appear at -3.10 and -1.27 eV, while the minority levels are at -1.54 and +0.43 eV with respect to the Fermi level of gold. None of the levels is within the experimental energy range and for this reason the Kondo temperature would be

an order of magnitude or more lower than for an isolated Co impurity. The antiferromagnetic configuration of the dimer has a very small energy difference with the ferromagnetic one, and the  $3d$  levels are also far from  $E_F$ . Therefore, the reason for not observing the narrow feature at  $E_f$  in the dimer case may be either that the Kondo temperature is too low or that the system is antiferromagnetic, in which case there would be no Kondo peak.

In summary, we have related results of LSDA calculations with features appearing near the Fermi level when transition metal atoms or clusters are adsorbed on Au(111). The proximity of the impurity  $d$  level with  $m = 0$  to the Fermi energy of the conduction band seems to be a necessary but not sufficient condition for observing an abrupt change in the tunneling current.

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TABLES

	Ti	V	Cr	Fe	Co	Ni
$\mu$	0.83	2.45	3.43	3.03	1.80	0.00
$E_{up} - E_f$	0.25	-0.02	-0.56	-2.50	-1.65	-0.30
$E_{dn} - E_f$	0.88	1.75	2.36	0.30	-0.06	-0.30

TABLE I. Magnetic moments (in Bohr magnetons) inside the muffin-tin sphere and position of the narrow energy bands with  $m = 0$  with respect to the Fermi energy (in eV).



## FIGURES

FIG. 1. Ti atom adsorbed on the Au(111) surface. Left) Partial densities of states in the muffin-tin sphere of the impurity. The full lines show all states of  $d$  symmetry while the dashed lines show the  $m = 0$  orbital only. Energies are in eV and referred to the Fermi level of Au. Right) Decay of the charge density into the vacuum, along the perpendicular to the (111) surface, starting on top of the adsorbed atom. Only states in two energy windows, close to the Fermi energy, are reported. Window  $w1$  is chosen so that it contains the  $d$  states with  $m = 0$ , window  $w2$  is next to it and both are 0.2 eV wide. The full line indicates majority spin density contribution within  $w1$ , the dashed line minority spin density contribution within  $w1$ , the dash-dot line minority contribution within  $w2$  and the dotted line majority contribution within  $w2$

FIG. 2. Same as Fig. 1 but for a V impurity.

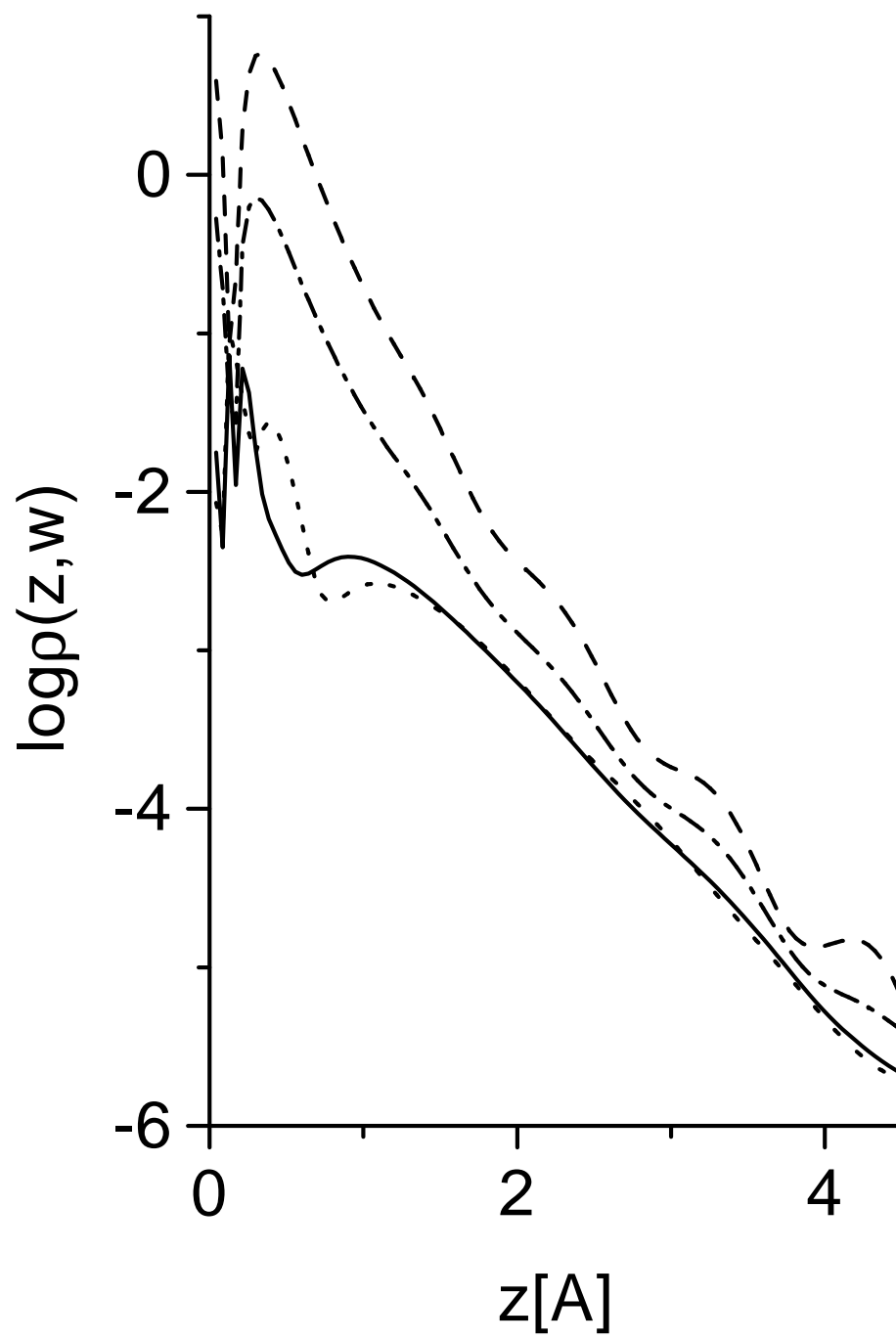
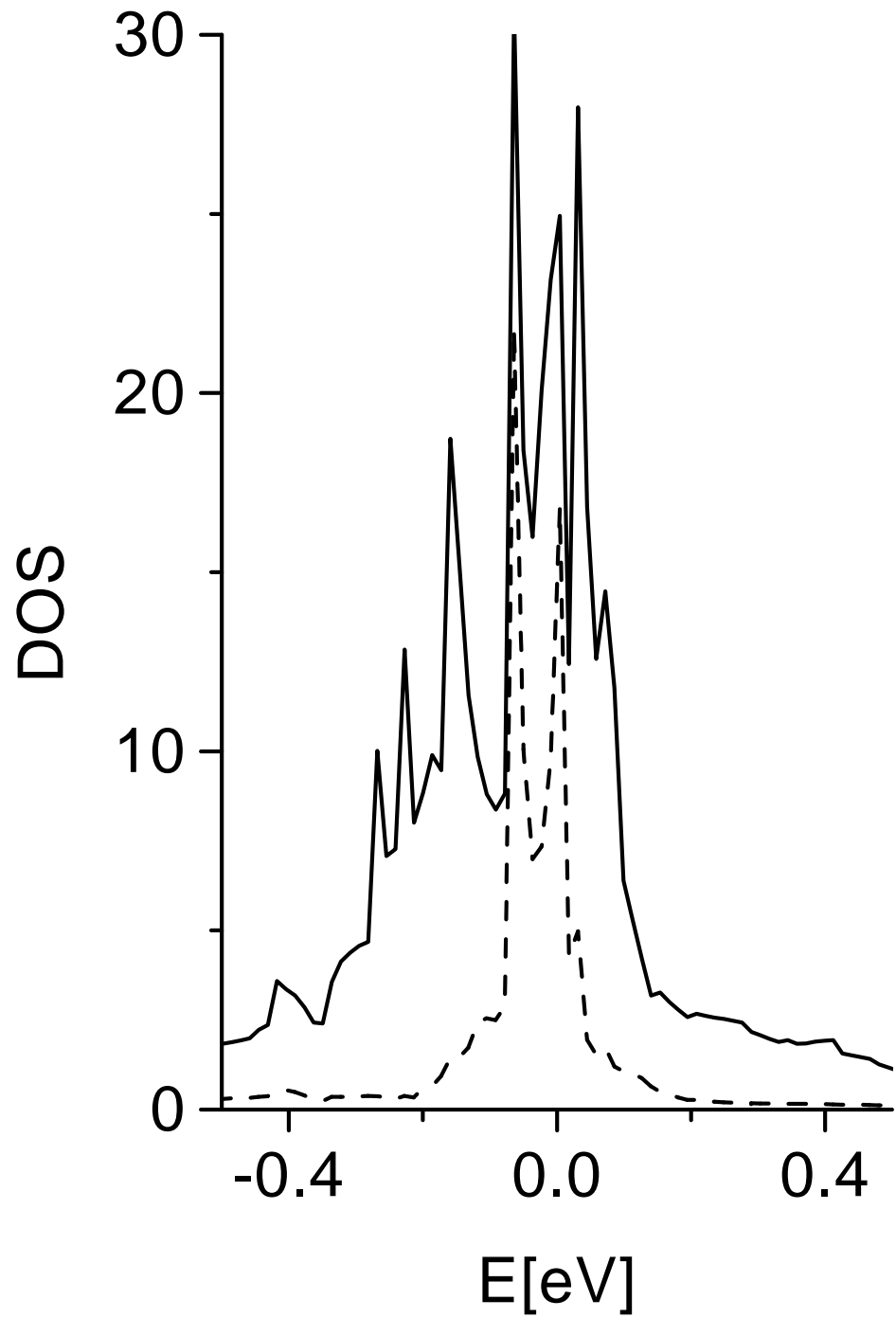
FIG. 3. Same as Fig. 1 but for a Cr impurity.

FIG. 4. Same as Fig. 1 but for a Fe impurity.

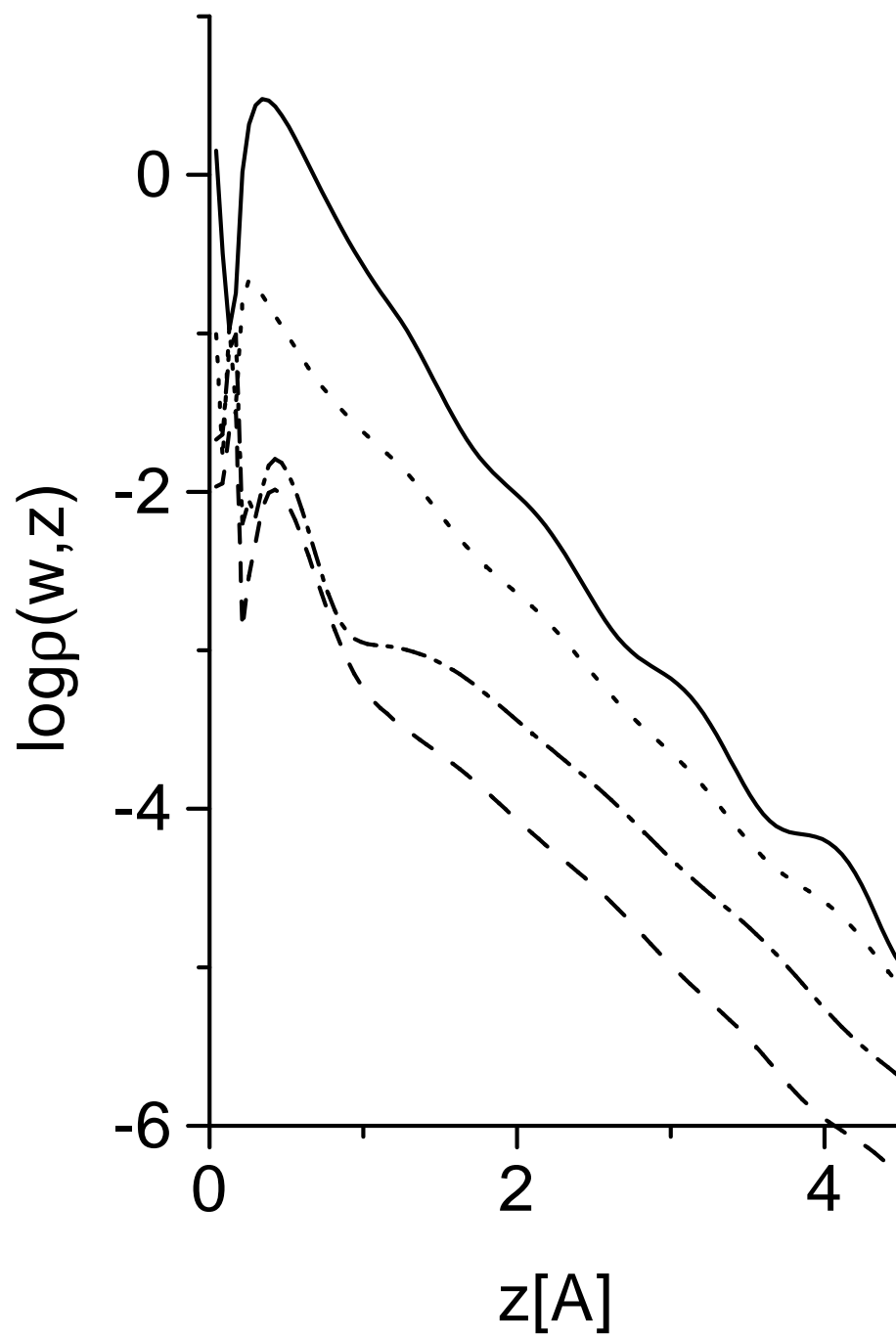
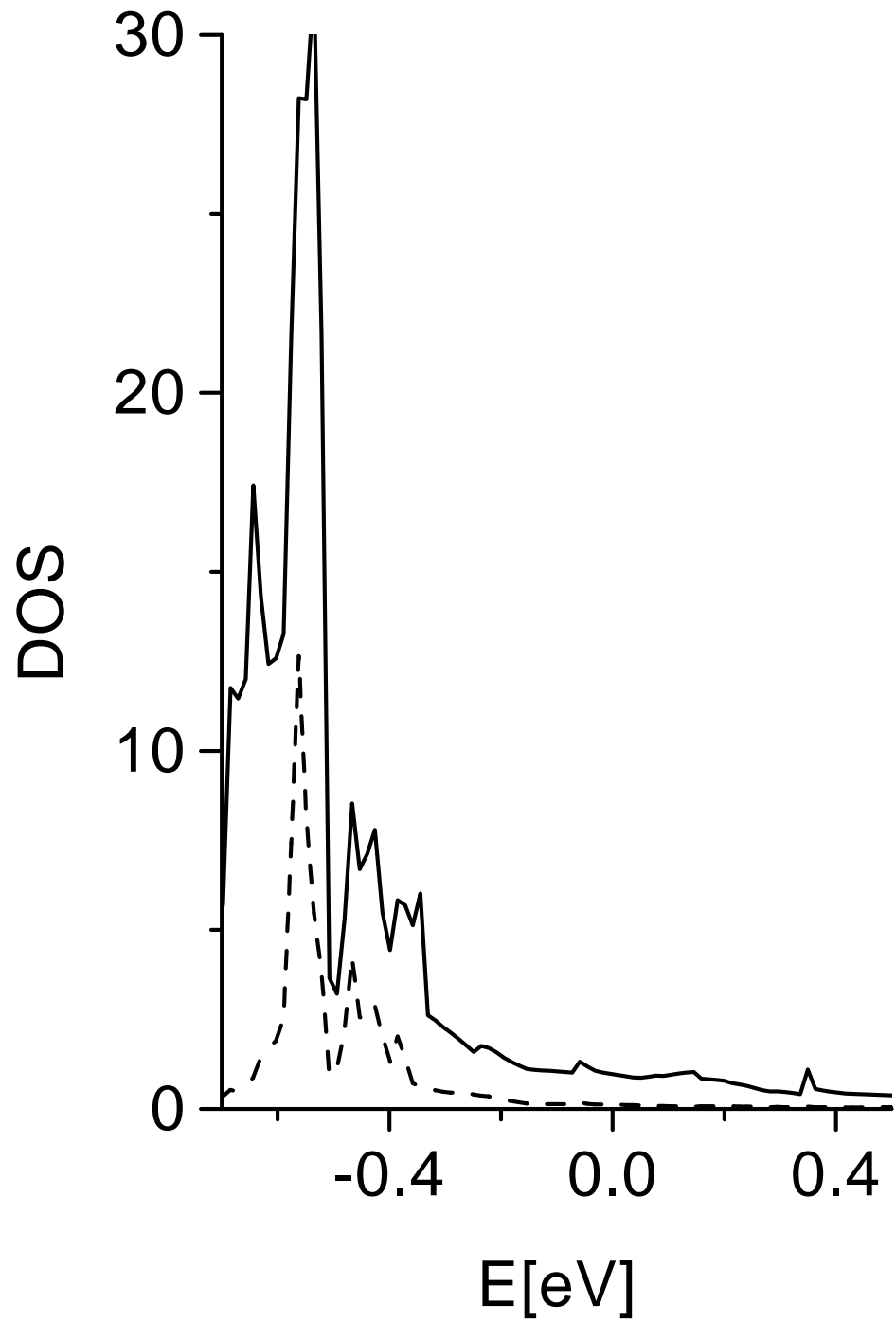
FIG. 5. Same as Fig. 1 but for a Co impurity.

FIG. 6. Same as Fig. 1 but for a Ni impurity.

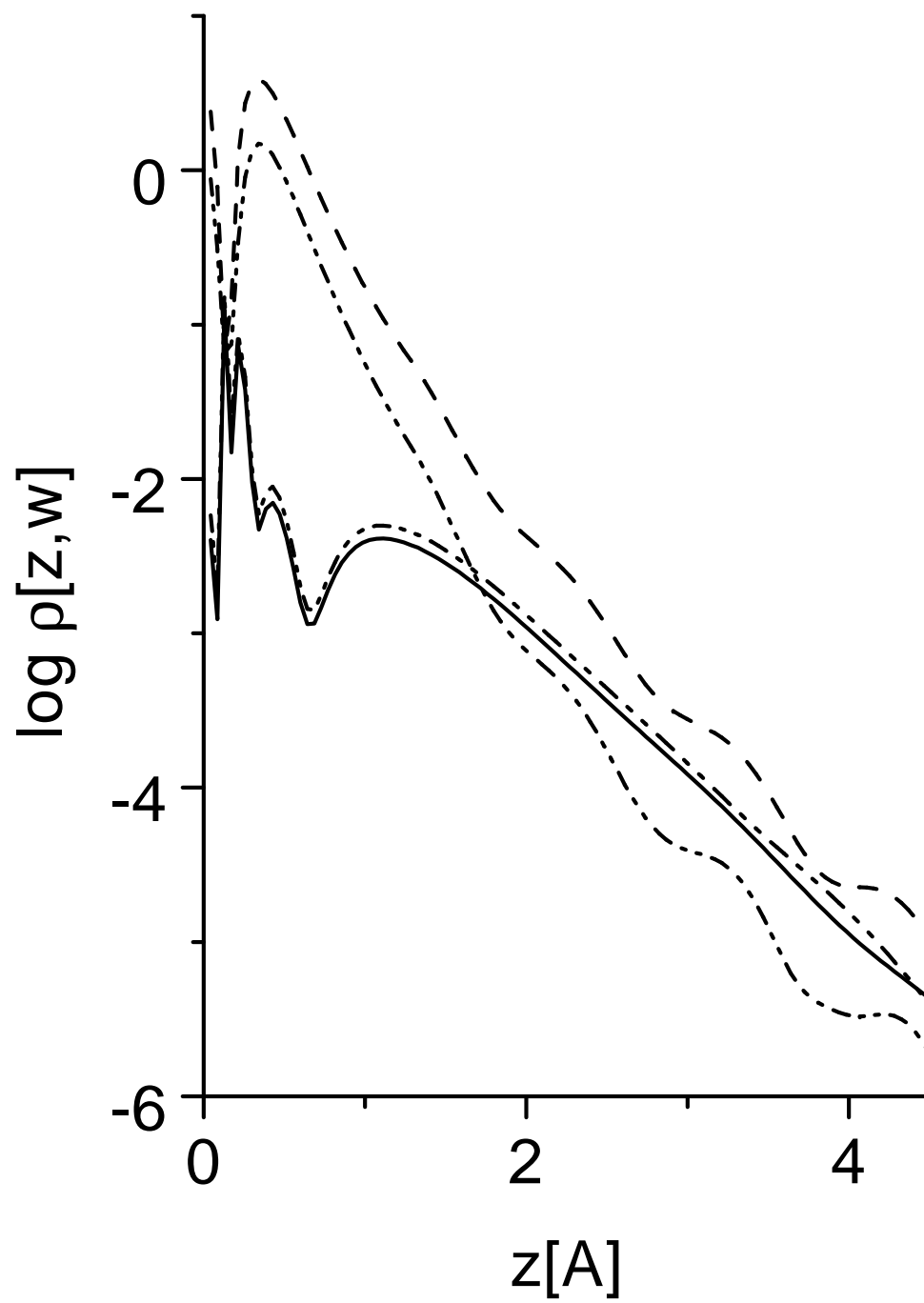
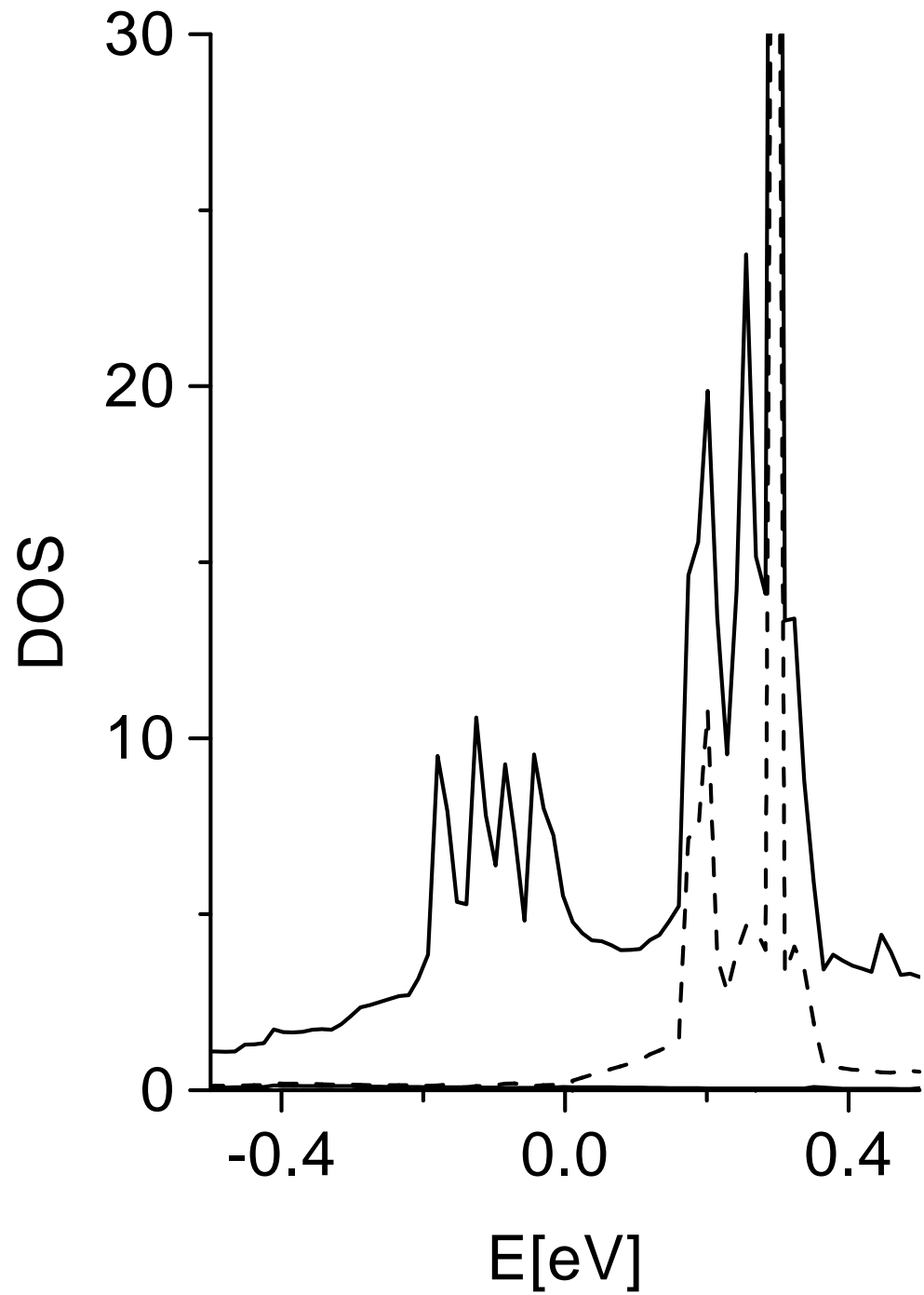
Co

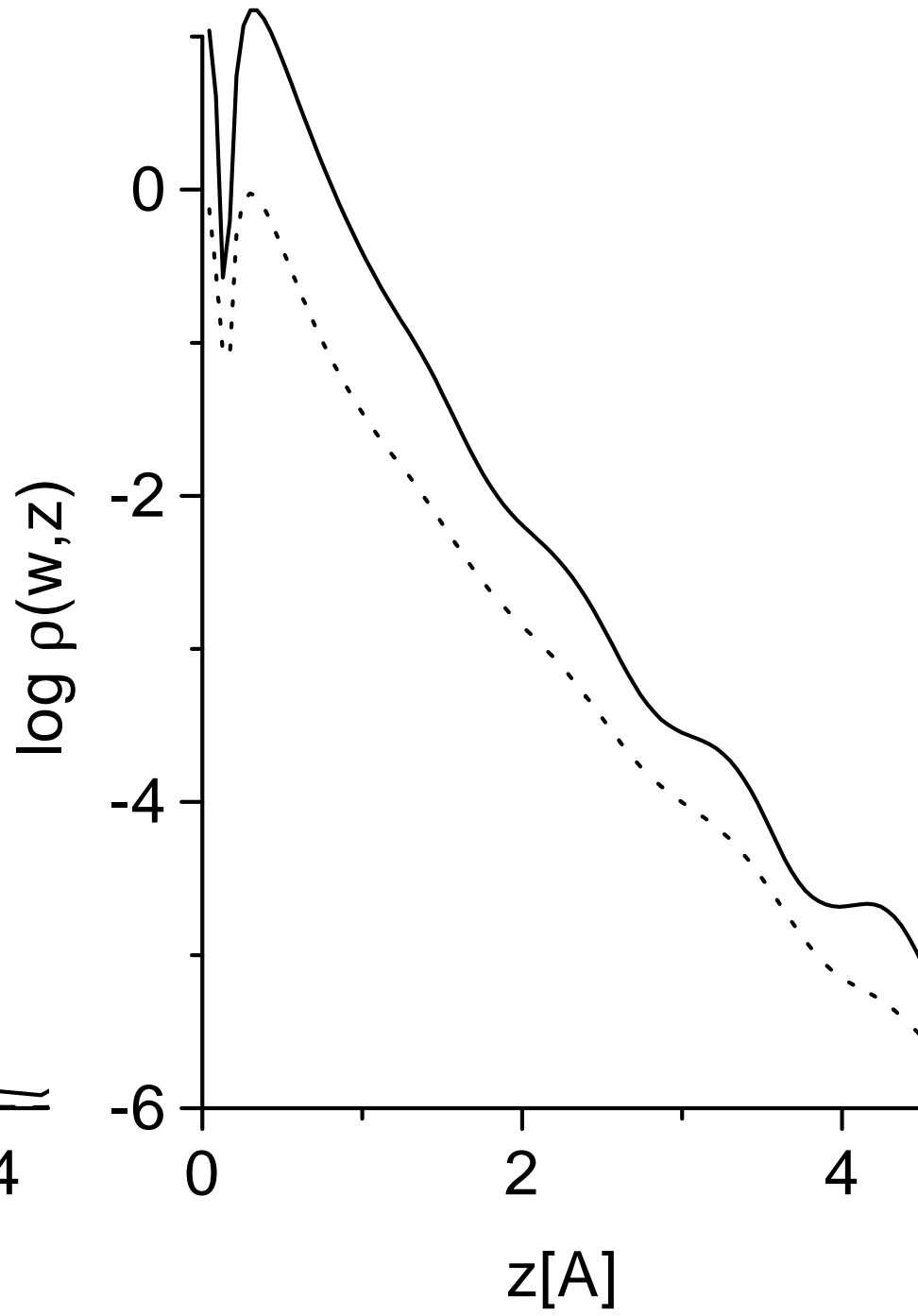
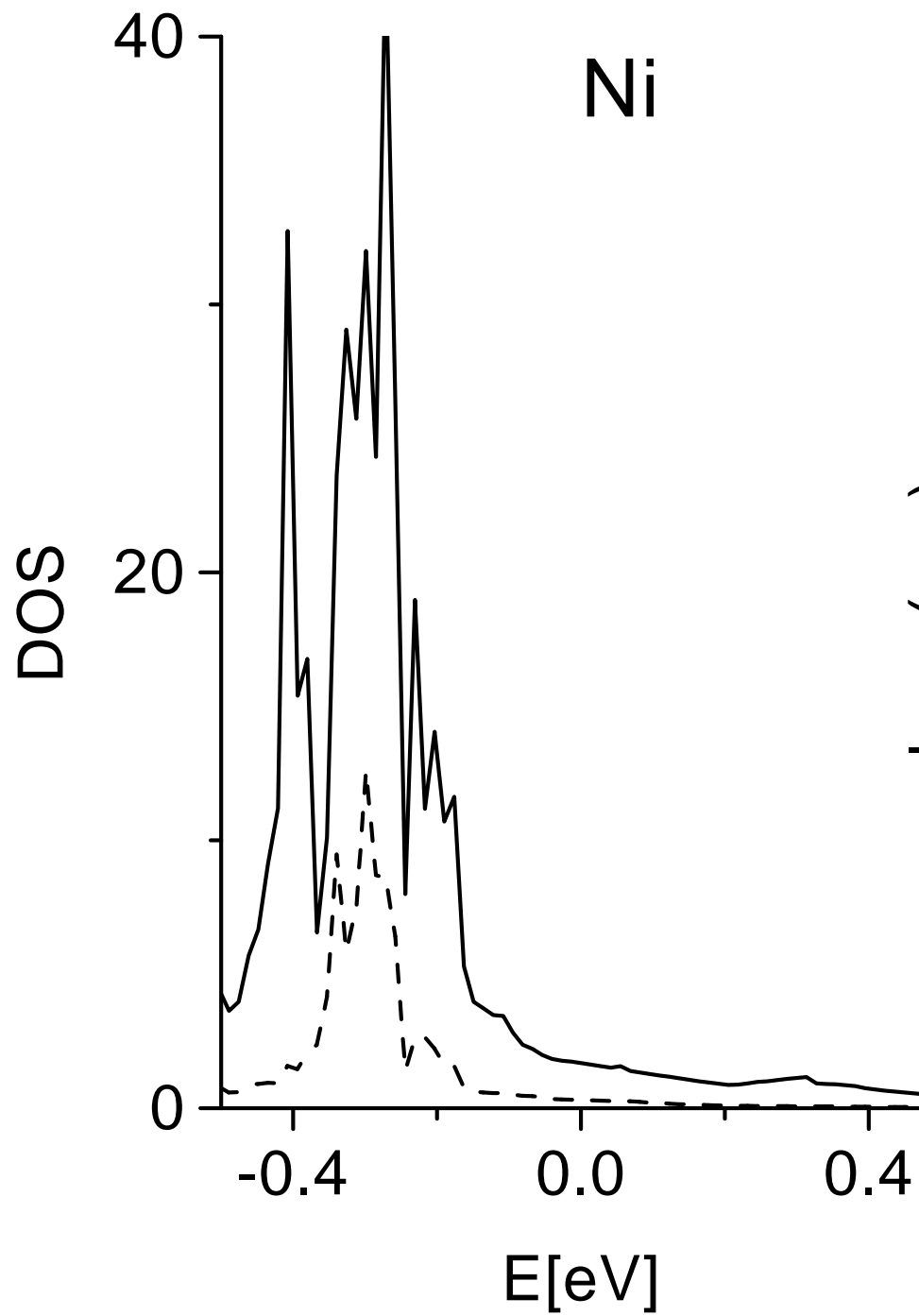


Cr

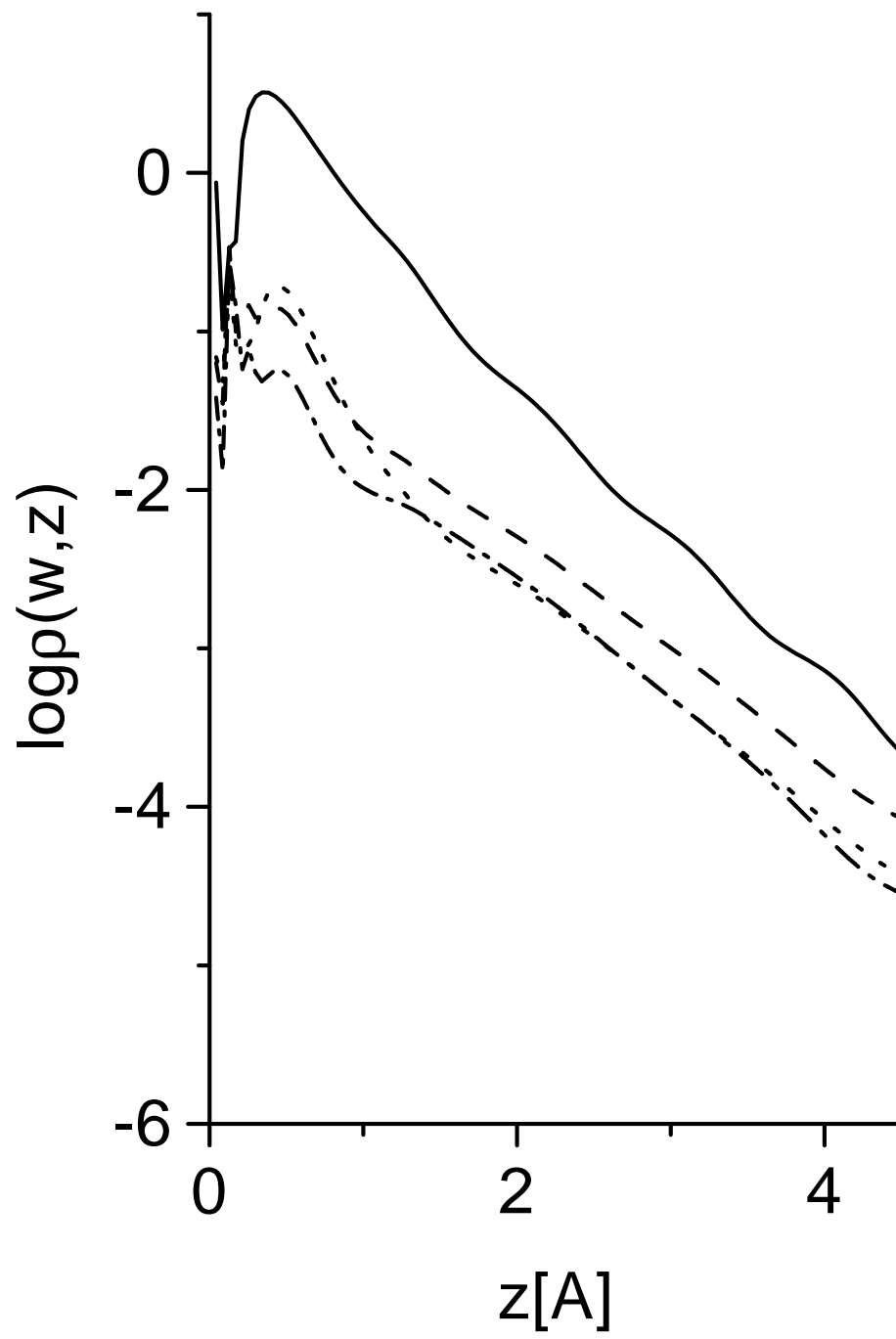
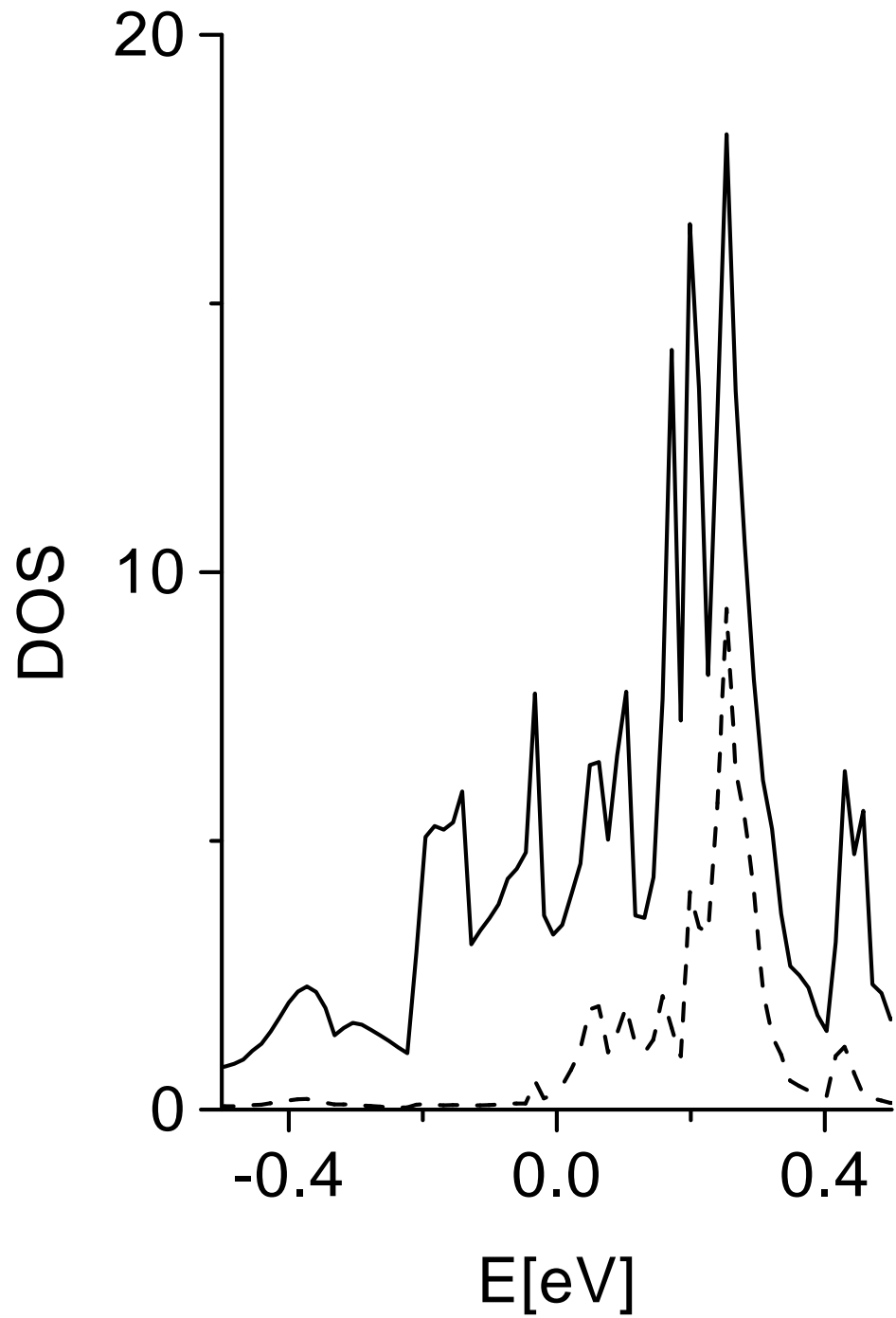


Fe





Ti



V

