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## Electronic structure and magnetic properties of aluminium clusters containing 3d impurity atoms

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**Abstract.** The electronic structure, local magnetic moments and magnetic susceptibility of Fe, Co and Ni substitutional impurities in Al clusters are calculated within the framework of the local spin-density approximation and the model of an ‘atom embedded in a jellium sphere’. Clusters containing up to 100 atoms are considered. It is obtained that the 3d impurities may be magnetic or non-magnetic depending on the Al cluster size. The impurity magnetic susceptibility is an oscillating function of cluster size that results from the size dependence of the position of the virtual bound states relative to the host Fermi energy. The magnetic susceptibility for Fe impurity atoms in Al clusters is positive, the magnetic susceptibility for Co atoms oscillates around zero, and the Ni impurity is diamagnetic. The results are in agreement with experimental data for dilute Al-based alloys.

### 1. Introduction

So far there is no agreed view of whether magnetic 3d impurities exist in Al. As is known, free 3d metal atoms carry a finite magnetic moment caused by Hund correlations between electrons of the unfilled 3d shell. However, these magnetic moments change considerably or vanish totally for dilute 3d impurities in metals, which results from interaction between the 3d electrons and conduction electrons of the host (see the Friedel–Anderson [1, 2] virtual-bound-state (VBS) model or the Schieffer–Hirst [3, 4] impurity-ion crystal-field model).

Previous investigations on the magnetic properties of 3d atoms in Al give inconsistent information. According to the experimental data reported by Grüner [5], 3d impurities, with the exception of Mn and Cr, are non-magnetic in Al; Al–Mn and Al–Cr exhibit spin-fluctuation properties. A local magnetic moment for Mn in Al has been observed, for instance, by Steiner *et al* [6] and by Cooper and Miljak [7]. Hauser *et al* [8, 9] and Youngquist *et al* [10] have found that Mn is magnetic in the quasi-crystalline icosahedral Al–Mn alloys (Mn content of 14 at.% or more) but non-magnetic in the orthorhombic phase. Moberly *et al* [11] measured the magnetization of dilute Al–Mn and Al–Fe alloys (with an impurity concentration of up to 0.023 at.%) and found that, if Mn and Fe impurities do have local magnetic moments, their values are very small ( $1.7 \times 10^{-2} \mu_B$  or less).

Previous theoretical studies of the electronic structure and magnetic properties of 3d impurities in Al have been of two types: calculations for finite clusters (see, e.g. [12–16]) and calculations for impurities embedded in the bulk solid (within an impurity-in-jellium model [17–19] and by Green function methods [20–23]). The majority of these calculations predict a magnetic ground state for Mn in Al [13–15, 19, 20]. From the Korringa–Kohn–Rostoker (KKR) Green function calculations of Deutz *et al* [20] it follows that not only Mn but also

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Cr and Fe have well defined local magnetic moments in the Al matrix ( $2.53\mu_B$ ,  $2.00\mu_B$  and  $1.78\mu_B$ , respectively). In their computations, only the impurity potential is perturbed; the potentials of the neighbouring host atoms are assumed to be unchanged. Recently, Guenzburger and Ellis [16] carried out first-principles spin-polarized cluster calculations of the electronic structure of Fe in Al, taking account of the lattice relaxation around the impurity, and found that the Fe atom in Al is non-magnetic.

In the present paper we consider the electronic structure, local magnetic moments and magnetic susceptibility of Fe, Co and Ni impurity atoms in Al clusters. Cluster calculations are traditionally employed in studies of surface and bulk materials. They help us to understand how the physical properties evolve from a free atom to a finite-sized system and bulk state. (However, it is to be noted that sometimes attempts to interpret the properties of a bulk object on the basis of calculations for separate clusters lead to discrepancies in the conclusions (see, e.g., cluster calculations for Mn in Al [13–15].) In recent years, microclusters themselves have become of great interest, because of the increase in the technological significance of their unique physical and chemical characteristics (see, e.g., [24–30]). Furthermore, lately methods to produce small clusters (containing up to a few hundred atoms) of controlled size have been developed [31, 32] and experiments on their properties have become possible.

Our calculations were carried out for clusters consisting of from five to 90 Al atoms and one central atom of Fe, Co or Ni. The model of an 'atom embedded in the centre of a spherical jellium cluster' and the density-functional theory [33, 34] in the local spin-density approximation of Vosko *et al* [35] were used. We have found that the electronic structure and magnetic properties of the impurities considerably change with increasing Al cluster radius. The 3d impurity atoms considered may be magnetic or non-magnetic depending on the cluster size. Note that previous investigations of Al–Mn alloys emphasize the great importance of the symmetry of 3d-atom sites for the formation of a local magnetic moment [8, 9, 13, 14]. We used the jellium approximation which neglects the cluster geometry and found that the size of the host system (if it is finite) also has an effect on the magnetic state of the impurity.

The plan of the rest of this paper is as follows. In section 2 the formalism for spin-polarized calculations of the electronic structure, local density of states, impurity magnetic moment and magnetic susceptibility for a spherical jellium cluster with an atom in the centre are described. The results obtained for Al clusters containing impurity atoms of Fe, Co and Ni are presented and discussed in section 3. The results are compared with theoretical and experimental data for point impurities of Fe, Co and Ni in bulk Al.

## 2. Model and formalism

### 2.1. Calculation of electronic structure

The electronic structure of Al as a simple metal is rather well described by a free-electron, or a jellium, model [36]. Although first-principles calculations [20] show that the density of states for Al near the Fermi energy somewhat differs from that for free electrons, and this leads to a deviation in the local density of states of transition-metal impurities in Al from the Lorentzian form predicted by the Friedel–Anderson [1, 2] vBS model for 3d impurities in a free-electron gas, numerous studies within the jellium approximation [17–19, 37] give results correctly reproducing (at least qualitatively) the experimental observed properties of dilute alloys of Al with 3d metals. A variety of jellium calculations for pure Al clusters

[38–40] also yields results which are in good agreement with first-principles approaches and experiments.

In the present calculations we consider Al clusters as jellium spheres with the embedded impurity atom in the centre. An electronic structure of Al jellium clusters containing the impurity atom in the centre was obtained within the framework of the spin-density functional theory from the self-consistent solution of the Kohn–Sham equations (atomic Rydberg units are used):

$$[-\nabla^2 + V^s(r)]\psi_{nls}(\mathbf{r}) = E_{nls}\psi_{nls}(\mathbf{r}) \quad (1)$$

$$V^s(r) = -\frac{2Z}{r} + 2 \int \frac{n^-(\mathbf{r}') - n^+(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}^s(r). \quad (2)$$

Here  $E_{nls}$  and  $\psi_{nls}$  are, respectively, one-electron energies and wavefunctions, the spin  $s = \uparrow, \downarrow$ ,  $Z$  is the nuclear charge of the impurity atom,

$$n^-(\mathbf{r}) = \sum_{nls} f_{nls} |\psi_{nls}(\mathbf{r})|^2$$

is the electron density of the jellium cluster with the impurity atom,  $f_{nls}$  is the occupation number of the state with the quantum numbers  $\{n, l, s\}$ , and the summation is over all states of the ‘atom-in-jellium’ system. The radial distribution of the positive jellium background is given by

$$n^+(r) = [3N_{\text{val}}^{\text{h}}(N_{\text{at}} - 1)/4\pi R^3]\theta(R - r)$$

where  $\theta(x)$  is the unit step function,  $N_{\text{at}}$  is the number of atoms in the cluster (including the impurity),  $N_{\text{val}}^{\text{h}}$  is the number of valence electrons in a host atom (for Al,  $N_{\text{val}}^{\text{h}} = 3$ ). The cluster radius  $R$  is found from the expression  $R = N_{\text{at}}^{1/3} r_{\text{c}}$ , where  $r_{\text{c}}$  is the atomic Wigner–Seitz (WS) radius (for Al,  $r_{\text{c}} = 2.98$  au).  $V_{xc}^s(r)$  is the local spin-polarized exchange–correlation potential (we used the form employed by Vosko *et al* [35]).

As is known, the addition of impurity atoms to a metal changes the density of states of the host system. These changes may be described in terms of the scattering characteristics of the impurity potential. For the isolated impurity in a free-electron gas the change in the density of states has the form [41]

$$\Delta d(E) = \frac{1}{\pi} \sum_{ls} (2l + 1) \frac{d\eta_{ls}(E)}{dE} \quad (3)$$

and the change in the integrated density of states is

$$\Delta N(E) = \frac{1}{\pi} \sum_{ls} (2l + 1) \eta_{ls}(E)$$

where  $\eta_{ls}$  is the difference between the impurity and host phase shifts:  $\eta_{ls} = \delta_{ls}^{\text{i}} - \delta_{ls}^{\text{h}}$ .

Then,  $\Delta N(E_{\text{F}})$  is the number of extra valence electrons due to the impurity ( $E_{\text{F}}$  denotes the Fermi energy of the host system). For the system as a whole to remain neutral,  $\Delta N(E_{\text{F}})$  should equal the perturbing charge connected with the impurity atom (Friedel sum rule), i.e.

$$\frac{1}{\pi} \sum_{ls} (2l + 1) \eta_{ls}(E_{\text{F}}) = \Delta Z^{\text{val}} \quad (4)$$

where  $\Delta Z^{\text{val}}$  is the difference between the impurity and host valencies.

If the impurity potential is strongly localized (as, for example, for 3d impurities), the Friedel sum rule (4) should be satisfied for phase shifts calculated at the impurity WS radius. This means that the perturbing impurity charge is completely screened by host conduction electrons inside the WS sphere.

In our calculations the impurity and host phase shifts were obtained through the use of the radial Kohn–Sham equation

$$[d^2/dr^2 - V_s^{\text{h,i}}(r) - l(l+1)/r^2 + E]\mathcal{P}_{l_s}^{\text{h,i}}(r, E) = 0$$

and the relation between radial wavefunctions  $\mathcal{P}_{l_s}^{\text{h,i}}(r, E)$  and phase shifts  $\delta_{l_s}^{\text{h,i}}$ , i.e.

$$\mathcal{P}_{l_s}^{\text{h,i}}(r, E) = \text{constant}[j_l(r, E) - \tan \delta_{l_s}^{\text{h,i}} n_l(r, E)]. \quad (5)$$

Here  $V^{\text{i}}(r)$  and  $V^{\text{h}}(r)$  are the self-consistent potentials of the jellium cluster with the 3d impurity and host atom, respectively, in the centre,  $V^{\text{h,i}}(r)$  is determined by (1) and (2) where, for  $V^{\text{i}}(r)$ ,  $Z$  is equal to the nuclear charge of the 3d impurity atom and, for  $V^{\text{h}}(r)$ ,  $Z$  has to be taken as the nuclear charge of the atom of the host system.

From (5), at  $r = r_c$ ,

$$\tan \delta_{l_s}^{\text{h,i}} = \{ \dot{j}_l(r_c, E) - [\dot{\mathcal{P}}_{l_s}^{\text{h,i}}(r_c, E)/\mathcal{P}_{l_s}^{\text{h,i}}(r_c, E)] j_l(r_c, E) \} / \{ \dot{n}_l(r_c, E) - [\dot{\mathcal{P}}_{l_s}^{\text{h,i}}(r_c, E)/\mathcal{P}_{l_s}^{\text{h,i}}(r_c, E)] n_l(r_c, E) \}$$

where

$$\dot{f}(r_c, E) = [\partial f(r, E)/\partial r]_{r=r_c}.$$

Here the energy is taken relative to the bottom of the spherical potential well of the pure jellium cluster (without any central atom). We considered  $E_F$  to be the highest occupied energy level of the pure jellium cluster.

## 2.2. Local magnetic moments and impurity magnetic susceptibility

Local magnetic moments on impurities were computed by integrating the spin density inside the WS sphere around the impurity atom:

$$M_{\text{loc}} = 4\pi \int_0^{r_c} [n_{\uparrow}^-(r) - n_{\downarrow}^-(r)] r^2 dr. \quad (6)$$

To calculate the magnetic susceptibility  $\Delta\chi$  due to the impurity atom, we employed the formalism constructed by Kohn and Luttinger [42] for dilute alloys with a nearly-free-electron host metal. If we neglect the spin–orbit interaction in the system,  $\Delta\chi$  can be written as the sum of orbital and spin parts, i.e.

$$\Delta\chi = \Delta\chi^{\text{orb}} + \Delta\chi^{\text{spin}}. \quad (7)$$

According to [42], the orbital contribution to the impurity magnetic susceptibility may be presented in the form

$$\Delta\chi^{\text{orb}} = \frac{c_{\text{imp}}}{\Omega_c} \left[ \left( \frac{e\hbar}{mc} \right)^2 \frac{1}{2} \sum_l \frac{(l+1)l}{6} \Delta d_l(E_F) - \frac{e^2}{6mc^2} \int \Delta n^-(r) r^2 dr \right] \quad (8)$$

where

$$\Delta d_l(E_F) = \frac{1}{\pi} \sum_s (2l+1) \left. \frac{d\eta_{ls}(E)}{dE} \right|_{E=E_F} \quad (9)$$

is the  $l$ th partial local density of states at  $E_F$ ,  $c_{\text{imp}} = N_{\text{imp}}/N_{\text{at}}$  is the concentration of impurity atoms,  $\Omega_c = \frac{4}{3}\pi r_c^3$  is the atomic WS volume and  $\Delta n^-(r) = n_{\text{imp}}^-(r) - n_{\text{host}}^-(r)$  is the change in the electron density due to the impurity atom.

The first term in equation (8) describes the orbital paramagnetic susceptibility of the impurity atom, and the second term gives the diamagnetic susceptibility and has the same form as the diamagnetic susceptibility of an isolated atom with the electron density  $\Delta n^-(r)$ .

For the spin part of  $\Delta\chi$  we used the well known expression for a Pauli paramagnetic susceptibility of non-interacting electrons:

$$\Delta\chi^{\text{spin}} = \frac{c_{\text{imp}}}{\Omega_c} \left( \frac{e\hbar}{mc} \right)^2 \frac{1}{4} \sum_l \Delta d_l(E_F). \quad (10)$$

The orbital paramagnetic susceptibility (the first term in (8)) and the spin paramagnetic susceptibility (10) are determined by the change in the scattering phase on the Fermi surface (see (9)) and, hence, they may be both positive and negative.

### 3. Results

Using the 'atom-in-jellium-sphere' model and the formalism described in section 2 we studied the electronic structure and magnetic properties of substitutional impurity atoms of Fe, Co and Ni in Al clusters.  $\text{Al}_n\text{Fe}$ ,  $\text{Al}_n\text{Co}$  and  $\text{Al}_n\text{Ni}$  clusters with  $n = 5, 10, 12, 18, 22, 29, 34, 43, 45, 55, 61, 65, 76, 83, 88$  and 90 were considered. We chose clusters containing these numbers of atoms because the jellium-sphere model for pure Al clusters of the same size has fully or nearly fully occupied electronic shells. In this case the Fermi energy of the host system, calculated with the local-density approximation, can be obtained more correctly [43].

As is known, localized d electrons in transition metals give a resonance in scattering phases at  $l = 2$ . As a 3d atom is the impurity in a metal host, the resonance corresponds to a VBS of d electrons. If the VBS lies near to the host Fermi energy, the host conduction electrons undergo strong scattering on the impurity. The d resonance determines many physical properties of point 3d defects. In the present paper we study how 3d impurity states behave in the finite Al matrix, how their occupation, localization and position relative to the host Fermi energy change with the host cluster size, and how that affects the magnetic properties of the impurity.

#### 3.1. Electronic structure

The electronic structure of Al jellium clusters with 3d impurities was obtained by self-consistently solving the Kohn–Sham equations (1) and (2). To determine the ground-state electronic configurations of clusters, we solved (1) and (2) for various occupation numbers of upper levels and, simultaneously, computed the total energy of the system. As the ground state we chose the configuration with the lowest total energy (this is given in more detail in [44]).

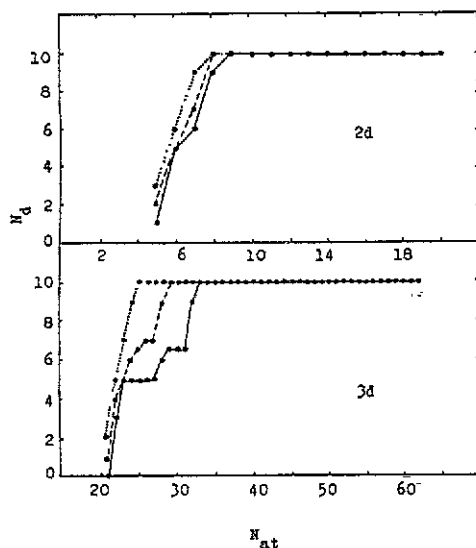


Figure 1. Dependence of the occupation of 2d and 3d shells of Al jellium clusters containing Fe (—), Co (---) and Ni (.....) atoms on the cluster size.

The calculations have shown that the spherical jellium cluster with the central 3d atom has the following energy spectrum. The five lowest energy levels are identical with those of a 3d atom core; the rest of them are similar to states in a spherical potential well. This order is broken by the localized d state in the upper part of the occupied energy region (table 1) (here the quantity  $n = n_n + 1$  has been considered as a principal quantum number of the state;  $n_n$  denotes the number of nodes of the wavefunction associated with the state). Surely, increasing the jellium-sphere size leads to the appearance of new electronic shells. However, as the new empty d state is filled, it is localized, while the previous d state is extended (this is discussed in detail in [44, 45]). As a result, the most localized d state is always the highest occupied state.

Table 1. Electronic configurations of Al jellium clusters containing the Fe impurity atom in the centre.

	Majority spin	Minority spin
	$1s^1 2s^1 1p^3 3s^1 2p^3 4s^1 3p^3 1d^5 \dots$	$1s^1 2s^1 1p^3 3s^1 2p^3 4s^1 3p^3 1d^5 \dots$
Al <sub>4</sub> Fe	$\dots 5s^1 2d^1$	$\dots 5s^0 2d^0$
Al <sub>5</sub> Fe	$\dots 2d^5 5s^0$	$\dots 5s^0 2d^0$
Al <sub>6</sub> Fe	$\dots 2d^5 5s^1$	$\dots 5s^1 2d^1$
Al <sub>8</sub> Fe	$\dots 5s^1 2d^5 1f^2$	$\dots 5s^1 2d^5 1f^0$
Al <sub>18</sub> Fe	$\dots 5s^1 1f^7 2d^5 4p^3 1g^9$	$\dots 5s^1 1f^7 2d^5 4p^3 1g^3$
	$\dots 5s^1 1f^7 2d^5 4p^3 1g^9$	$\dots 5s^1 1f^7 2d^5 4p^3 1g^9$
Al <sub>20</sub> Fe	$\dots 3d^0$	$\dots 3d^0$

In free 3d atoms the usual sequence of the filling of electronic states is broken, namely the 4s state is occupied before the 3d state. A similar inversion occurs during the filling of d states of Al jellium clusters containing the 3d atom. When the new d shell becomes half occupied, filling of the d state begins to alternate with filling of the next levels. So, as seen in figure 1, the number of electrons in the d levels increases more sharply up to the configuration  $d^5$  than from  $d^5$  to  $d^{10}$ . This effect is caused by the exchange interaction which promotes filling of the d level up to the configuration  $d^5$  and prevents it from  $d^5$  to  $d^{10}$ . As figure 1 shows, d levels are most rapidly filled in Al clusters containing the Ni atom and most slowly in systems with the Fe impurity.

## 3.2. Local magnetic moments of impurities

Using equation (6) we calculated the magnetic moments localized near the impurity atoms as a function of cluster size (table 2). The spin-density distribution for some Al jellium clusters containing the Fe, Co and Ni atom in the centre is presented in figure 2. As was expected, the systems with the partially occupied d shell have well defined local magnetic moments on the impurity. For clusters with completely occupied d shells the magnetic moments of 3d atoms are about zero. However, in some systems with closed d shells the magnetic moment inside the impurity WS sphere has a fairly large value (e.g.  $\text{Al}_{10}\text{Ni}$  and  $\text{Al}_{38}\text{Ni}$  (see table 2)). In this case the uncompensated spin was shown by the calculations of the spin-density distribution to belong to jellium electrons placed near the impurity atom. The enhanced spin density is outside the WS sphere of the impurity atom, occupying the small region inside  $r_c$  (see, e.g., the spin density of  $\text{Al}_{10}\text{Ni}$  in figure 2).

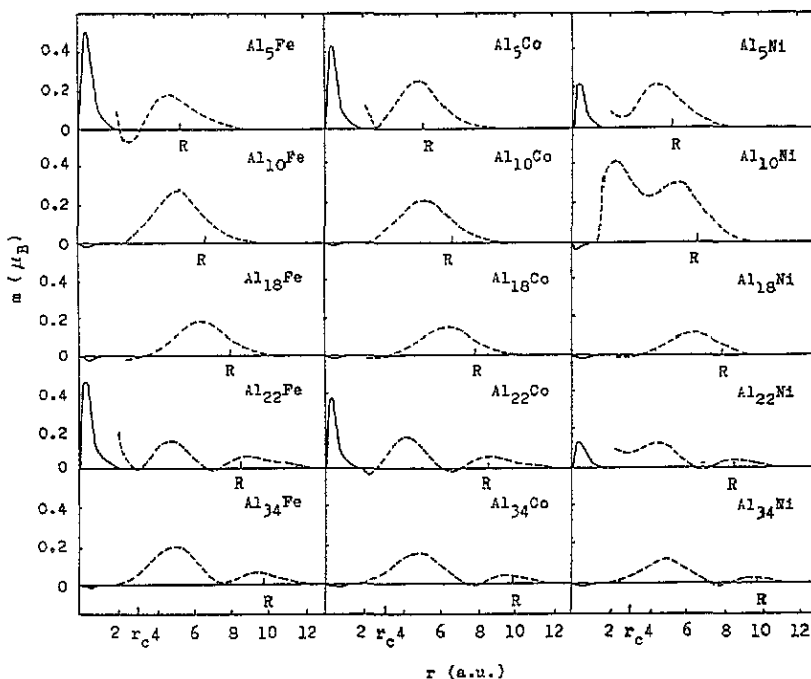


Figure 2. The radial spin-density distribution for Al jellium clusters containing Fe, Co and Ni atoms in the centre. The broken sections of the curves are represented on a larger scale (200:1).

Thus, 3d impurities have a local magnetic moment only in systems with partially occupied d shells. As seen in figure 1, such clusters are few. The d states in Al jellium clusters with the Fe impurity atom are filled more slowly than in the systems containing Co or Ni. So a magnetic state is more probable for the Fe impurity than for Co and Ni. In addition, the value of  $M_{loc}$  for Fe impurity atoms is the largest. This result agrees with the KKR Green function calculations of Deutz *et al* [20] who found Fe in Al to be magnetic ( $1.78\mu_B$ ). According to [20], the magnetic moments on Co and Ni disappear.



Table 2. Local magnetic moments on Fe, Co and Ni impurity atoms in Al clusters.

$N_{at}$	Fe		Co		Ni	
	Highest d state	$M_{loc}$ ( $\mu_B$ )	Highest d state	$M_{loc}$ ( $\mu_B$ )	Highest d state	$M_{loc}$ ( $\mu_B$ )
6	$2d_{\uparrow}^5 2d_{\downarrow}^0$	1.621	$2d_{\uparrow}^5 2d_{\downarrow}^0$	1.268	$2d_{\uparrow}^5 2d_{\downarrow}^1$	0.706
11	$2d_{\uparrow}^5 2d_{\downarrow}^5$	-0.057	$2d_{\uparrow}^5 2d_{\downarrow}^5$	-0.030	$2d_{\uparrow}^5 2d_{\downarrow}^5$	0.707
19	$2d_{\uparrow}^5 2d_{\downarrow}^5$	-0.089	$2d_{\uparrow}^5 2d_{\downarrow}^5$	-0.054	$2d_{\uparrow}^5 2d_{\downarrow}^5$	-0.032
23	$3d_{\uparrow}^5 3d_{\downarrow}^0$	1.633	$3d_{\uparrow}^5 3d_{\downarrow}^0$	0.931	$3d_{\uparrow}^5 3d_{\downarrow}^2$	0.495
30	$3d_{\uparrow}^5 3d_{\downarrow}^{1.5}$	1.332	$3d_{\uparrow}^5 3d_{\downarrow}^5$	-0.032	$3d_{\uparrow}^5 3d_{\downarrow}^5$	-0.024
35	$3d_{\uparrow}^5 3d_{\downarrow}^5$	-0.007	$3d_{\uparrow}^5 3d_{\downarrow}^5$	0.007	$3d_{\uparrow}^5 3d_{\downarrow}^5$	0.013
44	$3d_{\uparrow}^5 3d_{\downarrow}^5$	-0.062	$3d_{\uparrow}^5 3d_{\downarrow}^5$	-0.043	$3d_{\uparrow}^5 3d_{\downarrow}^5$	-0.029
56	$3d_{\uparrow}^5 3d_{\downarrow}^5$	-0.034	$3d_{\uparrow}^5 3d_{\downarrow}^5$	-0.029	$3d_{\uparrow}^5 3d_{\downarrow}^5$	-0.025
66	$4d_{\uparrow}^5 4d_{\downarrow}^0$	1.384	$4d_{\uparrow}^5 4d_{\downarrow}^0$	0.707	$4d_{\uparrow}^5 4d_{\downarrow}^0$	0.278
77	$4d_{\uparrow}^5 4d_{\downarrow}^4$	0.373	$4d_{\uparrow}^5 4d_{\downarrow}^5$	-0.068	$4d_{\uparrow}^5 4d_{\downarrow}^5$	-0.055
89	$4d_{\uparrow}^5 4d_{\downarrow}^5$	0.006	$4d_{\uparrow}^5 4d_{\downarrow}^5$	0.015	$4d_{\uparrow}^5 4d_{\downarrow}^5$	0.521

### 3.3. Local density of states

Local densities of states for Fe, Co and Ni impurity atoms in Al clusters of various sizes were calculated in terms of equation (3). The results are presented in figures 3–5. It is seen that the densities of states obtained resemble the VBS of the Friedel–Anderson model. However, for some clusters  $\Delta d(E)$  deviates appreciably from the Lorentzian shape. The discrepancy occurs for  $Al_nFe$  and  $Al_nCo$  clusters with the partially occupied localized d shell (e.g. for  $Al_5Fe$ ,  $Al_5Co$ ,  $Al_{22}Fe$ ,  $Al_{22}Co$  and  $Al_{29}Fe$  in figures 3 and 4). Their densities of states have an asymmetric structure which is most noticeable for the Fe impurity. The asymmetry of the VBS arises from the spin splitting of the localized d state. Note that Deutz *et al* [20] showed that, although Al is usually considered as a nearly-free-electron metal, the Lorentzian form of the VBS predicted by Anderson for 3d impurities in a free-electron gas is distorted if the VBS nearly coincides with critical points of the host band structure. We did not study the influence of the Al cluster geometry on the electronic and magnetic properties of 3d impurity atoms but suppose that this effect will be appreciable.

As seen clearly in the figures the position of the VBS with respect to the host Fermi energy non-monotonically changes with increasing Al cluster size. In table 3 are presented the difference  $E_d - E_F$  between the maximum of the local density of states and the Fermi energy for Fe, Co and Ni impurities in Al clusters as well as, for comparison, previous theoretical [17, 19–22] and experimental [6] results for isolated 3d impurities in bulk Al. The value of  $E_d - E_F$  for the Fe atom in Al clusters oscillates with size around that for the bulk matrix.  $E_d - E_F$  for Co and Ni impurities in Al clusters also non-monotonically changes with increasing cluster size. However, in these cases,  $E_d - E_F$  for all the Al clusters considered here is larger than that for Co and Ni impurities in bulk Al. Our results are closest to those of Mrosan and Lehmann [17] and it is not surprising because both they and we used the jellium approximation for a host metal.

Consider why the position of the VBS relative to the host Fermi energy changes with the cluster size. It was noted above (see section 3.1) that, as the next d level of the ‘3d-atom-in-jellium’ system is filled, the previous d state is extended. It can be represented as the gradual displacement of the localized d state to a higher energy (towards the Fermi level). When the highest d level has been occupied fully and shells above the d state are filled, this

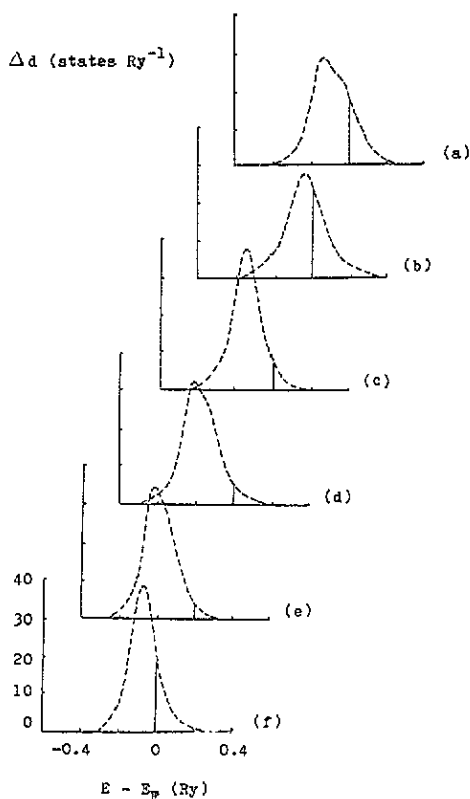


Figure 3. The change in local densities of states due to the impurity Fe atom for  $Al_nFe$  clusters; (a)  $n = 5$ ; (b)  $n = 10$ ; (c)  $n = 18$ ; (d)  $n = 22$ ; (e)  $n = 29$ ; (f)  $n = 43$ .

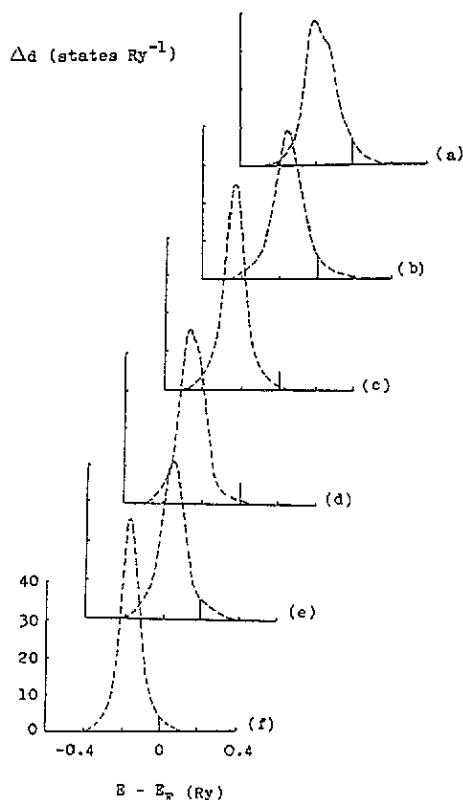


Figure 4. The change in local densities of states due to the impurity Co atom for  $Al_nCo$  clusters; (a)  $n = 5$ ; (b)  $n = 10$ ; (c)  $n = 18$ ; (d)  $n = 22$ ; (e)  $n = 29$ ; (f)  $n = 43$ .

d level sinks ('moves' away from the Fermi level). Then the new empty d level appears, and the localized d state again increases in energy, etc.

The size dependence of the position of the localized d state with respect to the Fermi energy leads to oscillations of the local density of states at  $E_F$  with a change in size.

Our results mean that all the properties of 3d impurities dependent on the change in the density of states at the Fermi level or determined by the resonant scattering of host conduction electrons on the VBS (such as the magnetic susceptibility, electronic specific heat, impurity resistivity and thermoelectric power) should non-monotonically change with change in the Al cluster size. Indeed, recently we have calculated the residual resistivity of 3d impurities in Al clusters [45] and revealed that it oscillates with changing cluster size. In the present work a similar result is obtained for the impurity magnetic susceptibility.

Note that, for some Al clusters with the Ni impurity,  $\Delta d(E_F)$  is negative (see figure 5), i.e. the substitution of Ni for Al decreases the local density of states at the Fermi level.

Figure 6 shows the change  $\Delta N(E_F)$  in the integrated density of states at the Fermi level, as a function of the cluster size.  $\Delta N(E_F)$ -values were calculated in terms of the phase shifts at the impurity WS surface. The horizontal broken lines indicate the differences  $\Delta Z^{\text{val}}$  between the impurity and host atomic valencies. The Friedel sum rule (4) is not satisfied for all the clusters considered. With increasing cluster size the value of  $\Delta N(E_F)$  oscillates around the corresponding  $\Delta Z^{\text{val}}$ . Apparently, the changes in the degree of

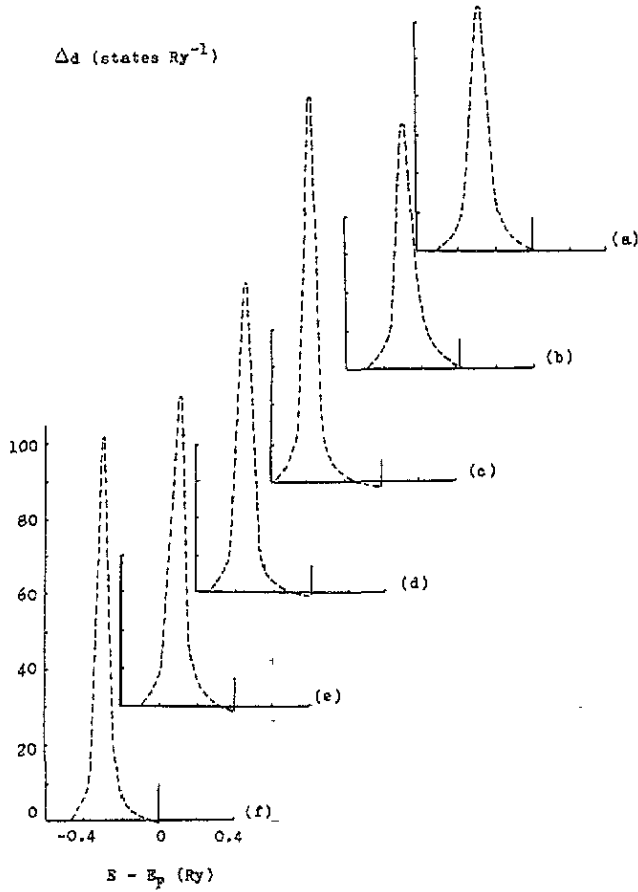


Figure 5. The change in local densities of states due to the impurity Ni atom for  $Al_nNi$  clusters; (a)  $n = 5$ ; (b)  $n = 10$ ; (c)  $n = 18$ ; (d)  $n = 22$ ; (e)  $n = 29$ ; (f)  $n = 43$ .

screening achieved for the 3d impurities in Al clusters of different sizes are caused by changes in the VBS position with respect to the host Fermi level.

Table 4 gives the additional local valence charge inside the impurity WS sphere which is calculated by integrating the difference between impurity and host valence electron densities over the WS sphere:

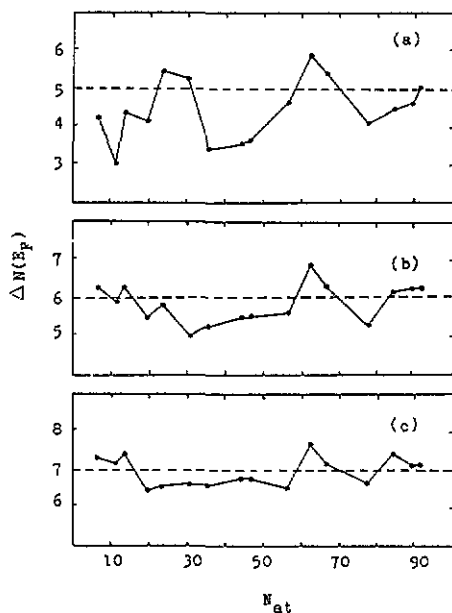
$$\Delta Q_{loc} = \int_{\Omega_c} \left[ \sum_{nls}^{val} f_{nls}^{imp} |\psi_{nls}^{imp}(r)|^2 - \sum_{nls}^{val} f_{nls}^{Al} |\psi_{nls}^{Al}(r)|^2 \right] dr$$

where the first sum is over all states of the '3d-impurity-in-Al-jellium-sphere' system with the exception of core shells of the impurity atom, the second sum is over all states of the Al jellium cluster containing the real Al atom in the centre except for the aluminium core states. The wavefunctions  $\psi_{nls}^{imp}$  and  $\psi_{nls}^{Al}$  are self-consistent solutions of the Kohn-Sham equations (1) and (2) for the Al jellium cluster with the 3d and Al atom, respectively, in the centre.

We found that, for all Al clusters and 3d impurities considered (except for  $Al_{10}Fe$  and  $Al_{10}Co$ ),  $\Delta Q_{loc}$  is somewhat greater than the corresponding  $\Delta Z^{val}$ . This is in agreement

**Table 3.** Position  $E_d - E_F$  of d resonances for Fe, Co and Ni impurities in Al.

Matrix	$E_d - E_F$ (Ryd) for the following impurities		
	Fe	Co	Ni
Al cluster, $N_{at} = 6$	-0.13	-0.20	-0.28
Al cluster, $N_{at} = 11$	-0.04	-0.15	-0.27
Al cluster, $N_{at} = 19$	-0.14	-0.23	-0.38
Al cluster, $N_{at} = 23$	-0.22	-0.27	-0.35
Al cluster, $N_{at} = 30$	-0.22	-0.14	-0.30
Al cluster, $N_{at} = 44$	-0.07	-0.15	-0.29
Al cluster, $N_{at} = 56$	-0.21	-0.30	-0.44
Al cluster, $N_{at} = 66$	-0.21	-0.24	-0.34
Al cluster, $N_{at} = 77$	-0.13	-0.19	-0.35
Al cluster, $N_{at} = 89$	-0.12	-0.22	-0.34
Bulk Al, impurity-in-jellium model [17]	-0.075	-0.135	-0.246
Bulk Al, spherical solid model [19]	-0.060	-0.088	-0.134
Bulk Al, KKR Green function method [20]	-0.059	-0.081	-0.132
Bulk Al, KKR Green function method [21]		-0.101	-0.132
Bulk Al, LMTO Green function method [22]	-0.030	-0.050	-0.101
Bulk Al, Experiment [6]	-0.066	-0.110	-0.176

**Figure 6.** The change in the integrated densities of states at the Fermi level for (a)  $Al_nFe$ ; (b)  $Al_nCo$ ; and (c)  $Al_nNi$  clusters as a function of cluster size. The horizontal broken lines indicate the differences  $\Delta Z^{val}$  between the impurity and host valencies.

with previous calculations for Fe, Co and Ni atoms in bulk Al [18, 20–23] and in Al clusters [12] and indicates a charge transfer from Al to the impurity atom.

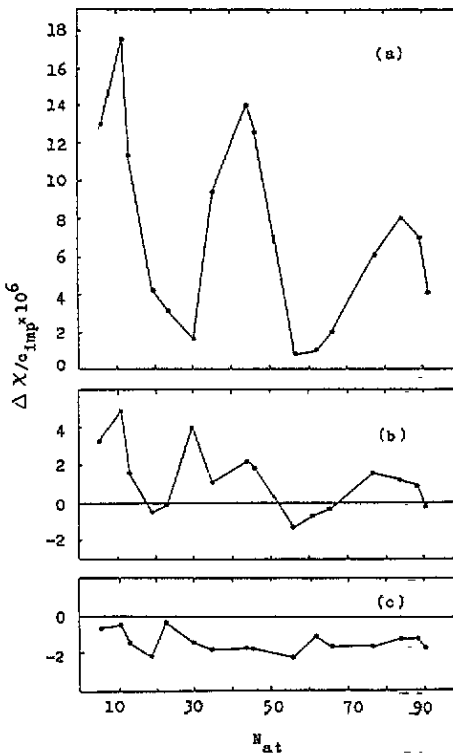
### 3.4. Magnetic susceptibility

The magnetic susceptibility of Fe, Co and Ni impurity atoms in Al clusters calculated in terms of equations (7)–(10) is plotted in figure 7. It is seen that  $\Delta\chi$  has an oscillating size dependence. A similar effect is known for thin films, the magnetic susceptibility of which oscillates depending on the film thickness [46, 47]. In figure 8 we show the orbital paramagnetic, spin paramagnetic and orbital diamagnetic components of the magnetic

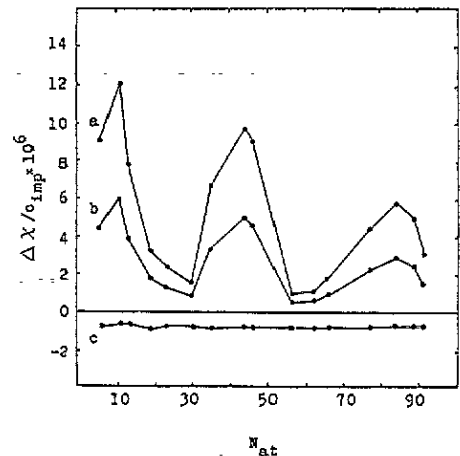
**Table 4.** Additional valence charges  $\Delta Q_{loc}$  localized inside the impurity Wigner-Seitz sphere for Fe, Co and Ni atoms in Al clusters.  $\Delta Z^{val}$  is the difference between the impurity and host valencies.

$N_{at}$	Fe, $\Delta Z^{val} = 5$	Co, $\Delta Z^{val} = 6$	Ni, $\Delta Z^{val} = 7$
6	5.12	6.28	7.27
11	5.00	5.92	7.11
19	5.38	6.42	7.40
23	5.18	6.30	7.23
30	5.24	6.38	7.28
44	5.29	6.33	7.31
56	5.30	6.34	7.32
66	5.21	6.28	7.25
77	5.33	6.35	7.34
84	5.05	6.02	7.04
89	5.06	6.10	7.13

susceptibility for the Fe impurity in Al clusters. It is obvious that the oscillating size dependence of the total  $\Delta\chi$  arises from oscillations of its paramagnetic (both orbital and spin) components. The diamagnetic susceptibility changes little.



**Figure 7.** The magnetic susceptibility of (a) Fe; (b) Co; and (c) Ni impurity atoms in Al clusters.



**Figure 8.** Orbital paramagnetic (curve a), spin paramagnetic (curve b) and orbital diamagnetic (curve c) components of the magnetic susceptibility for the Fe impurity in Al clusters.

According to equations (8) and (10) the paramagnetic susceptibility is determined by the change in the local density of states at the Fermi level. In the previous section we have shown that  $\Delta d(E_F)$  non-monotonically changes with cluster size. Hence oscillations appear in the size dependence of  $\Delta\chi$ . The oscillations of  $\Delta\chi$  are most pronounced for the Fe impurity and are faint for Ni. We noted above that oscillations of  $\Delta d(E_F)$  result from the change in the position of the vbs relative to the Fermi energy, which in turn is caused by periodic changes in the occupation of the localized d state with increasing cluster size (see sections 3.1 and 3.3). As seen in figure 1, d states are filled by electrons more slowly with increasing size for Al clusters with an Fe impurity than in systems containing Co and Ni. Therefore, for the Fe impurity the energy of the localized d state with respect to the Fermi level fluctuates most markedly, which results in the strong pronounced oscillations of the magnetic susceptibility.

The impurity magnetic susceptibility of Al clusters as a whole decreases when going from the Fe to the Ni impurity.  $\Delta\chi$  for Al clusters containing Fe atoms is positive.  $\Delta\chi$  for Al clusters with a Co impurity oscillates around zero. For the Ni impurity the magnetic susceptibility of all Al clusters considered is negative. Our results are in agreement with experimental data on the magnetic susceptibility for dilute alloys of Fe, Co and Ni in Al carried out by Sadoc [48]. In [48] for the Fe impurity the magnetic susceptibility was found to be positive, for the Co impurity the  $\Delta\chi$ -value was above zero, and the Ni impurity in bulk Al was found to be diamagnetic.

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