

THE ELECTRONIC STRUCTURE OF CUBO-OCTAHEDRAL AL_{13} AND $AL_{12}V$ CLUSTERS

By

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The electronic structure of a vanadium atom substituting for the central aluminium atom in a 13-atom cubo-octahedral cluster is calculated by the SCF- $X\alpha$ -SW cluster MO method. The electronic configurations of the central aluminium atom and of the central vanadium atom turn to be $(sp)^{3.06}(d)^{0.13}$ and $(sp)^{1.00}(d)^{3.98}(f)^{0.02}$, respectively.

The electronic structure of transition metal impurities alloyed in nonmagnetic metals has been studied for many years both experimentally and theoretically. Important results have been achieved recently by K. H. JOHNSON et al. [1] for transition metal impurities (Ni, Fe, Mn and V) alloyed in crystalline copper using the self-consistent-field $X\alpha$ scattered-wave (SCF- $X\alpha$ -SW) cluster molecular-orbital model.

The present work reports the electronic structure of a vanadium atom substituting for an aluminium atom in a 13-atom cubo-octahedral cluster. Though the size of this cluster is too small for describing satisfactorily the crystalline environment of the impurity [2], the main features, namely the local screening and the non-magnetic electronic configuration of the substituent vanadium atom, can be seen directly.

The geometry of the cubo-octahedral cluster of 13 atoms is shown in Fig. 1. This geometry corresponds to an atom (C) and its 12 nearest neighbours (N_1, N_2, \dots, N_{12}) in bulk aluminium of fcc structure with lattice constant $a=7.64$ au.

We have performed SCF- $X\alpha$ -SW cluster MO calculations for a "pure" aluminium cluster of 13 aluminium atoms with the geometry shown in Fig. 1. and for an "impure" cluster of 12 aluminium atoms in the nearest neighbour positions (N_1, N_2, \dots, N_{12}) and of a vanadium atom substituting for the central aluminium atom (C).

The muffin-tin version of the SCF- $X\alpha$ -SW cluster MO method is well documented [3—4]. The molecular field is partitioned into three types of muffin-tin regions: The atomic region consists of atomic spheres of radii $R=2.701$ au around each of the 13 atomic nuclei. The potential in the atomic spheres is taken to be spherically symmetric. The atomic region is enclosed in a sphere of radius $R_0=8.103$, the so-called outer sphere, centered at the central atomic nucleus. In the interatomic region, the region outside the atomic spheres and inside the outer sphere, the potential V_c is taken to be constant. The potential in the outer region, the region outside the

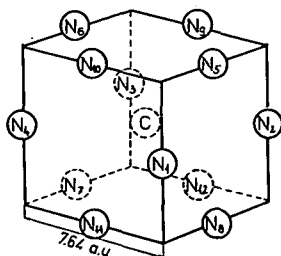


Fig. 1. The cubo-octahedral cluster of 13 atoms. This arrangement corresponds to an atom C and its 12 nearest neighbours N_1, N_2, \dots, N_{12} in a bulk fcc aluminium metal.

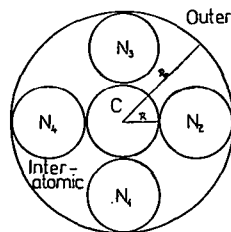


Fig. 2. The molecular field is partitioned into muffin-tin regions. C is the central region and N_1, N_2, N_3, N_4 are neighbour-regions.

outer sphere, is assumed to be spherically symmetric. The partitioned molecular field in the C $N_1 N_2$ plane is shown in Fig. 2.

In the calculations we have used the value $\alpha=1$ for the exchange parameter, since there is no unambiguous reason to prefer other choices [5—6], though for molecular calculations values proposed by SCHWARZ [7] are widely used with success.

The electronic energy levels for the cubo-octahedral Al_{13} and $Al_{12}V$ clusters are shown in Fig. 3. The orbital levels are labelled according to the irreducible representations of the cubic (O_h) point group.

The energies of the highest occupied levels, $3t_{1u}$ in both cases, are given by the values of -0.575 Ry and -0.569 Ry with occupation numbers 2 and 3 for Al_{13} and $Al_{12}V$, respectively.

For comparison, the bottom of the band $E(\Gamma_1)$, the muffin-tin constant V_c , and the Fermi energy E_F obtained by SEGALL [8] for bulk aluminium are also displayed on the energy-axis.

The energy difference of the highest occupied and the lowest levels, the "occupied band width", is greater for the pure cluster (0.66 Ry) than for the impure one (0.60 Ry), though much less than for bulk aluminium (0.81 Ry [6]). Nevertheless, calculations on aluminium clusters performed by SALAHUB and MESSMER [2] show that a cluster containing 43 atoms yields an occupied band-width of 99% of the bulk band-width.

The distribution of the 39 valence electrons in the molecular orbitals for the pure cluster Al_{13} is given in Table I. For the impure cluster $Al_{12}V$,

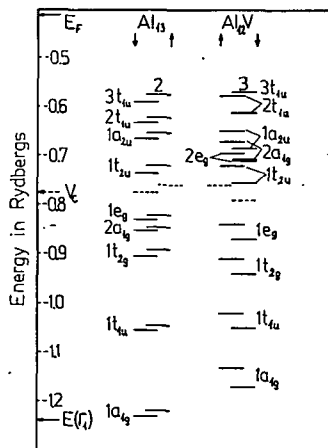


Fig. 3. Energy levels of the pure Al_{13} and of the impure $Al_{12}V$ clusters. The notation of the irreducible representations of the cubic (O_h) point group is used to label spin-up and spin-down states. The highest occupied levels are marked by their occupancies. The bottom of the band, the muffin-tin constant V_c and the Fermi energy E_F calculated by SEGALL [8] are given on the energy-axis.

Table I

Occupied spin-up (\uparrow) and spin-down (\downarrow) orbitals, occupancy and energy of orbitals and distribution of 39 electrons in each of the orbitals, among various regions (central C, neighbour N, interatomic and outer) of the pure Al_{13} cluster

| Orbital | | Occupancy | Energy | Q(C) | Q(N) | Q(inter) | Q(out) |
|------------|--------------|-----------|--------|-------|-------|----------|--------|
| 3 t_{1u} | \uparrow | 2 | -0.575 | 0.013 | 0.046 | 0.383 | 0.048 |
| | \downarrow | 3 | -0.588 | 0.015 | 0.046 | 0.383 | 0.048 |
| 2 t_{1u} | \uparrow | 3 | -0.624 | 0.217 | 0.036 | 0.278 | 0.069 |
| | \downarrow | 3 | -0.634 | 0.209 | 0.037 | 0.281 | 0.069 |
| 1 a_{2u} | \uparrow | 1 | -0.653 | 0.000 | 0.053 | 0.324 | 0.041 |
| | \downarrow | 1 | -0.666 | 0.000 | 0.053 | 0.325 | 0.040 |
| 1 t_{2u} | \uparrow | 3 | -0.722 | 0.000 | 0.064 | 0.180 | 0.056 |
| | \downarrow | 3 | -0.734 | 0.000 | 0.064 | 0.181 | 0.055 |
| 1 e_g | \uparrow | 2 | -0.816 | 0.011 | 0.056 | 0.281 | 0.031 |
| | \downarrow | 2 | -0.829 | 0.010 | 0.056 | 0.281 | 0.031 |
| 2 a_{1g} | \uparrow | 1 | -0.846 | 0.322 | 0.033 | 0.234 | 0.042 |
| | \downarrow | 1 | -0.853 | 0.325 | 0.033 | 0.236 | 0.042 |
| 1 t_{1g} | \uparrow | 3 | -0.891 | 0.014 | 0.061 | 0.221 | 0.029 |
| | \downarrow | 3 | -0.904 | 0.014 | 0.061 | 0.222 | 0.029 |
| 1 t_{1a} | \uparrow | 3 | -1.043 | 0.078 | 0.056 | 0.240 | 0.013 |
| | \downarrow | 3 | -1.055 | 0.076 | 0.056 | 0.241 | 0.013 |
| 1 a_{1g} | \uparrow | 1 | -1.223 | 0.307 | 0.039 | 0.217 | 0.003 |
| | \downarrow | 1 | -1.232 | 0.297 | 0.040 | 0.219 | 0.003 |

the 41 electrons are distributed among various regions of the cluster as displayed in Table II.

A comparison of Table I and II shows the effect of substituting a vanadium atom for the central aluminium atom. Namely, (i) there appears a new energy level $2 e_g$ of d character at -0.7 Ry which is highly localized to the central vanadium atom (2.6 electrons in the central region C), (ii) there is a tendency towards localization of electrons in d-like $1 t_{2g}$ and $1 e_g$ orbitals to the central region, (iii) the electrons in the s-like $1 s_{1g}$ and p-like $2 t_{1u}$ states are pushed out of the central region, and that happens, though to a somewhat moderate extent, to the electrons in the s-like $2 a_{1g}$ and p-like $1 t_{1u}$ states, as well, (iv) there is a pronounced raise of 0.14 Ry in the energy of the s-like $2 a_{1g}$ state, resulting a decrease in the "density of states" in the energy range -0.85 — -0.80 Ry, (v) the spin-splitting of the energy levels is

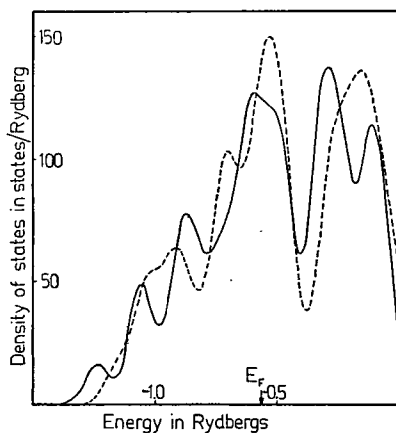


Fig. 4. The density of states calculated by broadening the discrete energy levels with Gaussian functions for the pure (solid line) and for the impure (dashed line) clusters. The broadening parameter σ was chosen to be 0.05 Ry in both cases.

Table II

Occupied spin-up (\uparrow) and spin-down (\downarrow) orbitals, occupancy and energy of orbitals and distribution of 41 electrons in each of the orbitals among various regions (central C, neighbour N, interatomic and outer) of the impure $Al_{12}V$ cluster

| Orbital | Occupancy | Energy | Q(C) | Q(N) | Q(inter) | Q(out) |
|-------------------------|-----------|--------|-------|-------|----------|--------|
| 3 t_{1u} \downarrow | 3 | -0.569 | 0.076 | 0.045 | 0.299 | 0.081 |
| 2 t_{1u} \uparrow | 3 | -0.578 | 0.008 | 0.047 | 0.379 | 0.048 |
| | 3 | -0.613 | 0.008 | 0.047 | 0.380 | 0.047 |
| 1 a_{2u} \uparrow | 1 | -0.651 | 0.002 | 0.053 | 0.321 | 0.040 |
| | 1 | -0.686 | 0.002 | 0.052 | 0.322 | 0.047 |
| 2 a_{1g} \uparrow | 1 | -0.671 | 0.178 | 0.037 | 0.300 | 0.076 |
| | 1 | -0.707 | 0.178 | 0.037 | 0.301 | 0.075 |
| 2 e_g \uparrow | 2 | -0.695 | 0.629 | 0.018 | 0.131 | 0.018 |
| | 2 | -0.708 | 0.647 | 0.016 | 0.144 | 0.013 |
| 1 t_{2u} \uparrow | 3 | -0.719 | 0.002 | 0.064 | 0.179 | 0.054 |
| | 3 | -0.753 | 0.002 | 0.064 | 0.180 | 0.054 |
| 1 e_g \uparrow | 2 | -0.839 | 0.198 | 0.045 | 0.244 | 0.020 |
| | 2 | -0.869 | 0.152 | 0.048 | 0.254 | 0.022 |
| 1 t_{2g} \uparrow | 3 | -0.910 | 0.133 | 0.054 | 0.200 | 0.021 |
| | 3 | -0.942 | 0.111 | 0.055 | 0.205 | 0.022 |
| 1 t_{1u} \uparrow | 3 | -1.016 | 0.031 | 0.059 | 0.243 | 0.017 |
| | 3 | -1.051 | 0.032 | 0.059 | 0.243 | 0.017 |
| 1 a_{1g} \uparrow | 1 | -1.133 | 0.088 | 0.055 | 0.242 | 0.008 |
| | 1 | -1.169 | 0.089 | 0.055 | 0.243 | 0.008 |

three times greater for the impure cluster (0.03 Ry) than for the pure one (0.01 Ry), with the exception of the "impurity level" $2e_g$, for which its value is of 0.01 Ry.

By broadening the discrete energy levels ε_i , with Gaussian functions, "density of states" for the pure and impure cluster have been calculated according to the form

$$N(E) = \sum_i n_i \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(E-\varepsilon_i)^2}{2\sigma^2}\right].$$

In this expression, n_i is the occupation number of the energy level ε_i , and σ is a broadening parameter. The densities of states for the pure and impure clusters are plotted in Fig. 4.

The distribution of electrons among the various regions of the cluster is given in Table III. Though the number of spin-up electrons exceeds that of the spin-down electrons by 1 for the pure and by 3 for the impure cluster, because integer occupation numbers have been used in the calculations, no net resultant spin exists in the central region. The screening of the central atomic nucleus is completed in its muffin-tin region.

As to the electronic configuration of the central atom, the number of electrons in orbitals of different symmetry are listed in Table IV. The notations of the dominant

Table III

The number of spin-down (n_{\downarrow}) and spin-up (n_{\uparrow}) electrons in various regions of the pure Al_{13} and impure $Al_{12}V$ clusters

| Region | number of electrons | | n_{\downarrow} | n_{\uparrow} | $n_{\downarrow} - n_{\uparrow}$ | $n_{\downarrow} + n_{\uparrow}$ |
|-------------|---------------------|--------|------------------|----------------|---------------------------------|---------------------------------|
| | Central | Al | (Pure) | 6.58 | 6.60 | -0.02 |
| V | | (Imp) | 11.55 | 11.44 | 0.11 | 23.00 |
| Neighbour | Al | (Pure) | 6.03 | 5.98 | 0.05 | 12.01 |
| | Al | (Imp) | 6.08 | 5.94 | 0.14 | 12.03 |
| Interatomic | | (Pure) | 5.27 | 4.86 | 0.41 | 10.13 |
| | | (Imp) | 5.58 | 4.62 | 0.97 | 10.20 |
| Outer | | (Pure) | 0.79 | 0.75 | 0.05 | 1.54 |
| | | (Imp) | 0.86 | 0.62 | 0.24 | 1.48 |

Table IV

The number of electrons in the central region in orbitals of different symmetry and of different angular momentum s,p,d and f for the pure (Al) and for the impure (V) cluster. The electronic configuration of the central Al is $(sp)^{3.08}(d)^{0.13}$ and of the central V is $s(p)^{1.00}(d)^{3.98}(f)^{0.02}$

| | | n_{\downarrow} | n_{\uparrow} | $n_{\downarrow} - n_{\uparrow}$ | $n_{\downarrow} + n_{\uparrow}$ |
|-------------|----|------------------|----------------|---------------------------------|---------------------------------|
| $a_{1g}(s)$ | Al | 0.622 | 0.629 | -0.007 | 1.251 |
| | V | 0.267 | 0.266 | 0.001 | 0.533 |
| $t_{1u}(p)$ | Al | 0.900 | 0.911 | -0.011 | 1.811 |
| | V | 0.348 | 0.117 | 0.231 | 0.465 |
| $e_g(d)$ | Al | 0.020 | 0.022 | -0.002 | 0.042 |
| | V | 1.598 | 1.654 | -0.056 | 3.252 |
| $t_{2g}(d)$ | Al | 0.042 | 0.042 | 0.000 | 0.084 |
| | V | 0.333 | 0.399 | -0.066 | 0.732 |
| $t_{2u}(f)$ | Al | 0.000 | 0.000 | 0.000 | 0.000 |
| | V | 0.006 | 0.006 | 0.000 | 0.012 |
| $a_{2u}(f)$ | Al | 0.000 | 0.000 | 0.000 | 0.000 |
| | V | 0.002 | 0.002 | 0.000 | 0.004 |
| sp | Al | 1.522 | 1.540 | -0.018 | 3.062 |
| | V | 0.615 | 0.383 | 0.232 | 0.998 |
| d | Al | 0.062 | 0.064 | -0.002 | 0.126 |
| | V | 1.931 | 2.053 | -0.122 | 3.984 |
| f | Al | 0.000 | 0.000 | 0.000 | 0.000 |
| | V | 0.008 | 0.008 | 0.000 | 0.016 |

partial wave components are also shown. Adding up the various contributions the electronic configuration of the central aluminium atom turns to be $(sp)^{3.06}(d)^{0.13}$, and $(sp)^{1.00}(d)^{3.98}(f)^{0.02}$ for the central vanadium atom.

Finally, it should be noted, that our calculation can not be compared directly with the results on transition metal impurities in aluminium metals, first because the "renormalizing effect" of the crystalline environment can not be described satisfactorily by the first shell of neighbouring atoms for a free-electron-like metal such as aluminium [1, 2]. Furthermore, lattice distortion is not included, as well.

Nevertheless, our results are consistent with and show the main features of the electronic structure of a substitutional vanadium impurity in bulk aluminium metal.

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ЭЛЕКТРОННАЯ СТРУКТУРА КУБО-ОКТАЭДРИЧЕСКИХ КЛАСТЕРОВ Al₁₃ И Al₁₂V

И. К. Дзьемант

Вычислена электронная структура атома ванадия, замещенного вместо центрального атома кубо-октаэдрического, кластера алюминия кластерным методом многократного рассеяния в $X\alpha$ -приближении самосогласованного поля. Электронные конфигурации центрального атома алюминия и атома ванадия оказались $(sp)^{3.06}(d)^{0.13}$ и $(sp)^{1.00}(d)^{3.98}(f)^{0.02}$ соответственно.