STABILITY OF POSITIVELY CHARGED METALLIC CLUSTERS

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The Coulomb explosion of positively charged metallic clusters is studied. The observed stability of multiply positively charged spherical Pb_n clusters can be explained by assuming that metallic-like screening begins to occur in clusters with approximately 30 or more atoms and becomes bulk-like in clusters with approximately 300 atoms or more. Also, results for the stability of two-fold positively charged transition-metal clusters are given.

Despite intensive research the electronic properties of small metallic clusters are still not very well understood. For example, the optical, magnetic and chemical properties and metallic behaviour of small clusters are presently not well understood [1]. In what small cluster sizes does screening of electric charges occur? A change from metallic- to insulating-like behaviour may occur for decreasing cluster size [2] ‡. This would have important consequences for many properties and might also be relevant for metal–insulator transitions in liquids or vapors (Cs, Rb and Hg)[2]. A further important question with respect to chemical properties is, how does the cluster geometry change for increasing cluster size? It is shown in the following that the study of the stability of charged small clusters sheds some light on these questions.

Recently, the stability of Pb_n^{m+} clusters consisting of n atoms and which have been m-fold positively charged by electron impact collision has been studied [3]. One observes stable Pb_n^{2+} clusters for $7 \leqslant n \leqslant 13$ and again for $n > 30$. Three-fold positively charged clusters Pb_n^{3+} are stable for $n \gtrsim 45$. Pb_n^{4+} clusters are stable, if they have more than 60 to 70 atoms. For transition-metal clusters one observed stable Ni_3^{2+} clusters, but Cu_3^{2+} are unstable, for example [4].

In order to explain these experimental results, we use the following criterion for the stability [5] of clusters M_n:

$$E_{\mathrm{coh,s}} = \delta E_{\mathrm{C}} \,. \tag{1}$$

Here, $E_{\mathrm{coh,s}}$ is the cohesion energy of a surface atom and δE_{C} the change of the Coulomb energy upon emitting a positively charged surface atom. $E_{\mathrm{coh,s}}$ may be determined by using experimentally derived bond energies or by calculation using a tight-binding type theory [5]. Approximately [5], $E_{\mathrm{coh,s}} = (Z_s/Z_b)^{1/2} E_{\mathrm{coh,b}}$, where Z is the coordination number and b refers to the bulk. δE_{C} is calculated [5] by using the Coulomb potential $V(R) = \mathrm{e}^{-\lambda R}/R$ with screening length λ^{-1}. R refers to the distance between the charges assumed to be localized. The criterion $E_{\mathrm{coh,s}} = \delta E_{\mathrm{C}}(R)$, eq. (1), yields results, as illustrated in fig. 1, for the critical number of atoms for which the charged clusters be-

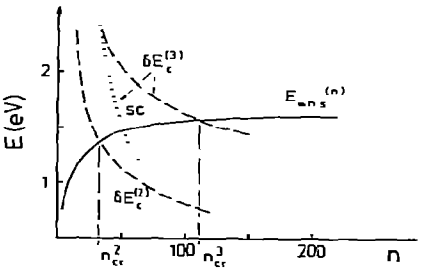

Fig. 1. Illustration of the graphical determination of n_{cr}. The curve labelled sc. refers to screened Coulomb interaction.

‡ Assuming that a coordination number larger than 6 is necessary for metallic-like behaviour, the bulk-like screening is expected to begin in Pb_n, Hg_n, etc. for $n > 30$ to 40 atoms.

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Table 1
Results for the critical number of atoms, n_{cr}, for which charged spherical (fcc-like) clusters M_n^{m+} are stable, calculated from eq. (1). The point-like positive charges are put at equal maximal distance at the surface. The experimental results are from ref. [3]

M_n^{m+}	n_{cr}(calc)		n_{cr}(exp)
	no screening	screened Coulomb interaction	
Pb_n^{2+}	30	31	30
Pb_n^{3+}	130	49	45
Pb_n^{4+}	325	61	≈ 72
Pb_n^{5+}	500	≈ 70	–
Ni_n^{2+}	≈8	–	–
Ni_n^{3+}	30	30	–
Ni_n^{4+}	≳ 100	≈ 40 (to 50)	–

come stable. Note, for spherical clusters with radius R we use $R \propto n^{1/3}$.

In order to demonstrate that the stability of charged clusters depends sensitively on the screening of the charges by the valence electrons, we performed calculations by assuming bare Coulomb interactions and also by assuming alternatively that bulk-like screening begins to occur gradually in clusters having 30 atoms or more. Results for spherical clusters are shown in table 1. For Ni_n we use data given in ref. [6]. For Pb_n we use [7] for the interatomic distance $d = 3$ Å and for the bulk screening parameter $\lambda_b = 1.8$ Å^{-1}. $\lambda = 0$ describes no screening of the positive charges. For the screening we use the following model. In small clusters having less than 30 atoms we assume no screening, e.g. $\lambda = 0$. For clusters M_n with $n \geqslant 30$ atoms we assume that $\lambda \to \lambda_b$ linearly with $\lambda \approx \lambda_b$ from $n \geqslant 300$ atoms. Such a gradual increase of the screening is expected on general physical grounds and also suggested (for s,p-type metals) by the density dependence of the metal–insulator transition in Hg, etc. [2]. The physical situation expected for $\lambda^{-1} \propto N(0)$ is illustrated in fig. 2. The electronic density of states at the Fermi energy is denoted by $N(0)$.

First, we discuss the results for Pb_n given in table 1. Comparing the numerical results presented in table 1 with experimental results for Pb_n clusters [3] and for Ni_n clusters [4], we conclude that our model, assuming for Pb_n clusters a gradual increase in screening for clusters having 30 or more atoms, can explain the experimental results obtained for larger clusters. It is interesting to note, that using $\lambda = \lambda_b$ for very small Pb_n clusters would yield stable Pb_2^{2+}, Pb_3^{3+}, etc. clusters. Furthermore, using the screening model $\lambda = 0$ for $n \lesssim 30$ and $\lambda = \lambda_b$ for $n \gtrsim 30$, e.g. assuming a sudden increase in screening, one obtains from eq. (1) that Pb_n^{3+}, Pb_n^{4+}, Pb_n^{5+} are all stable from $n \approx 35$ on. All these results suggest that λ must be smaller than λ_b in small Pb clusters. Of course, this is plausible on general physical grounds. Clearly, one does not expect for very small clusters bulk-like screening of electric charges or conducting-sphere like behaviour ($\lambda = \lambda_b$). That bulk-like screening will occur gradually for Pb_n, Hg_n, etc. clusters from approximately 30 atoms on is suggested by the density dependence of the metal–insulator transition in Hg, etc. [2]. Generally, $\lambda^{-1} \propto N(0)$ and the electron density of states at the Fermi energy $N(0)$, should depend sensitivily on the average coordination number of the atoms, in particular for s,p-type electron bonds (see fig. 2).

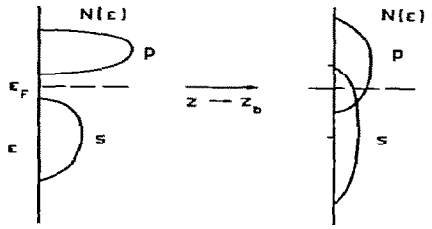

Fig. 2. Illustration of the dependence of the s,p-electron density of states, $N(\epsilon)$, on atomic coordination number z. such behaviour is expected for Pb_n, Hg_n, etc. clusters. The mean coordination number Z approaches its bulk value Z_b as the size of the cluster increases.

That stable Pb_n^{2+} clusters are observed for [3] $7 \leqslant n \leqslant 13$ in contrast to our numerical results obtained for spherical clusters suggest that those Pb_n^{2+} clusters are not spherical in shape. Indeed, assuming linearly shaped Pb_n clusters, we calculate for Pb_n^{2+} the critical size $n_{cr} = 6$, if we use $E_{coh,s} = 0.84$ eV which we calculated previously and which is the experimentally observed energy for dimers [4]. On general physical grounds we expect that linear clusters cease to exist for larger numbers of atoms. This might be the reason why stable Pb_n^{2+} are only observed for $7 \leqslant n \leqslant 13$.

Discussing now the results for n_{cr} given in table 1

for spherical Ni_n clusters, we note that, in contrast to experiment, observing stable Ni_3^{2+} our screening model (and also $\lambda = 0$) yields $n_{cr} \approx 8$ Again, assuming that charged small transition-metal clusters are linear in shape, we calculate from eq. (1) with $\lambda = 0$ that Ni_3^{2+}, M_3^{2+} (M = Fe, Co, Pt, Au), but not Ag_3^{2+} and Cu_3^{2+}, are stable, in agreement with experiment [4]. We calculate Cu_4^{2+} to be stable Assuming $\lambda = \lambda_b$ for all clusters, we calculate all transition-metal and noble-metal clusters M_3^{2+} to be stable. These results suggest that small charged transition-metal clusters should be linear in shape and that screening in such small clusters is poorer than in larger clusters

Summarizing our numerical results obtained from eq. (1), we conclude that there is evidence for poor screening of electric charges in very small transition-metal clusters and in Pb_n clusters with $n < 30$. Furthermore, our analysis suggests that very small charged clusters M_n^{m+} are linear in shape These tentative conclusions, if correct, are of general importance for many properties and should be checked by further experiments and calculations [‡‡]. In view of calculations studying the metal–insulator transition in s,p-type metals as a function of coordination number [2], one expects metallic-like screening to begin in Pb clusters having approximately 30 atoms or more. Presumably this happens smoothly and thus we assumed for simplicity that λ increases for $n \geqslant 30$ linearly towards λ_b for increasing cluster size. Assuming $\lambda = \lambda_b$ for n = 300 to 400 atoms yields the best agreement with experiment This seems reasonable, since for such cluster sizes the number of surface atoms with low coordination number is sufficiently smaller than the number of bulk atoms.

While we expect similar screening behaviour for Hg_n clusters, different behaviour may result for simple metal clusters like Na_n or for transition-metal clusters where d-electrons also contribute to screening

However, also for those clusters, one expects on general physical grounds that the screening length λ^{-1} is, in small clusters having only 2 to 3 atomic shells (n = 20 to 30 atoms), much larger than in the bulk solid. It would be interesting to check this by experiments.

[‡‡] For example, use a one-electron local density theory for small clusters and assume the same core-hole screening as in bulk material.

We do not expect $E_{coh}(Pb)$ to depend strongly on the charge m+[‡]. For Ni_n^{m+}, Cu_n^{m+}, etc., this may be different. Shifts of s,p and d electrons (if $N_d < 10$) to larger binding, resulting from an increase in the attractive Coulomb potential of the atoms in charged clusters, tend to stabilize M_n^{2+}. In our calculations this has been neglected. Increased binding for $M_n \rightarrow M_n^{m+}$ may be particularly important for rare-gas clusters, since in M_n^{m+} the rare-gas electronic configuration is perturbed, which will cause larger cohesion.

[‡] The criterion for the stability of charged clusters, eq. (1), should include image charge effects, etc., which may play a role during the emission of a charged atom. Thus, $E_{coh,s}$ should be the effective energy necessary for emission of an atom.

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