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STRUCTURAL AND ELECTRONIC PROPERTIES OF SMALL METAL AGGREGATES

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INTRODUCTION

A coherent picture of the geometrical structure of Van der Waals clusters, and in particular of rare gas atom clusters is now emerging. There are both reliable electron diffraction data [1] for clusters in a beam having between 10 and 1000 atoms and good molecular dynamic calculations, using for example a Lennard-Jones potential, which predict diffraction patterns in good agreement with the observed one's.

The situation for metal clusters is not as favourable. There is virtually no experimental data on the geometrical structure of aggregates having between 10 and ~ 300 atoms, i.e. for aggregates with a diameter less than $\sim 20 \text{ \AA}$. Our knowledge of the geometrical structure of very small aggregates is furthermore indirect and only partial. The theoretical situation is a little better, although it is difficult to perform good ab-initio calculations in the intermediate size range where neither the standard theoretical methods of the infinite bulk nor the usual quantum chemistry methods apply [2].

This paper is divided into two parts: in the first part we review the informations obtained by electron microscopy and electron diffraction techniques on the structure of aggregates of diameter larger than $\sim 20 \text{ \AA}$, and we describe the results of simple models. In the second part we focus on very small alkali metal aggregates and we compare some of the available experimental data with calculations of their structural and electronic properties. The evolution of the properties of alkali metal clusters as a function of size is certainly not representative of all metal aggregates (see e.g. ref. 3). They are, however, the metal clusters for which we have the most complete experimental data.

GEOMETRICAL STRUCTURE OF FCC METAL AGGREGATES OF DIAMETER LARGER THAN $\sim 20 \text{ \AA}$

At thermodynamic equilibrium, the shape of a crystal is obtained by minimizing the free energy $F = F_b + \sum_i \gamma_i A_i$ at constant volume where F_b is supposed to be extensive, γ_i and A_i are respectively the surface tension and the area of the face i of a crystal. This minimising leads to the famous Curie-Wulff equation $\gamma_i/h_i = \text{const}$, where h_i is the distance between the face i and a central point. In the case of f.c.c. metals, in which we are particularly interested, the relations $\gamma_{[110]}/\gamma_{[111]} > \sqrt{\frac{3}{2}}$ and $\gamma_{[100]}/\gamma_{[111]} > \sqrt{\frac{3}{2}}$ generally hold, and this leads to the crystal shape given in fig. 1a. When $\gamma_{[100]}/\gamma_{[111]} < \sqrt{\frac{3}{2}}$, the Curie-Wulff equation leads to the cubooctahedron given in fig. 1b.

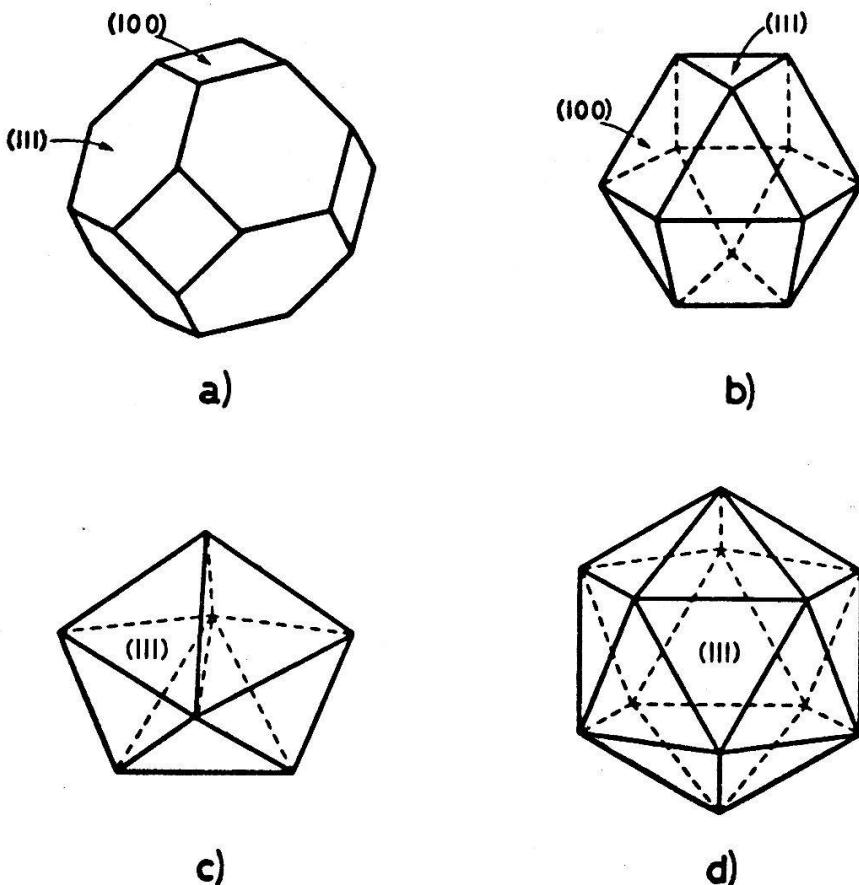


Figure 1 : a) cubooctahedron with (111) hexagonal faces or truncated octahedron, b) cubooctahedron with (111) triangular faces, c) decahedron, d) icosahedron. Notice the five-fold symmetry of c) and d).

The comparison between the predicted Curie-Wulff shape and the experimental data is difficult, in particular since the interaction with the support cannot be neglected and since it is not always clear that the observed shape is an equilibrium shape rather than the result of the growth process. In the case of Platinum all the electron microscopy results indicate that most of the small aggregates of diameter larger than 20 Å or even smaller are single microcrystals. The shape of the aggregates is more difficult to obtain. One method is to use the weak beam dark field technique [4], which shows thickness fringes which allow the three dimensional shape of the particle to be determined. For example, Yacaman et al. [5] have identified the shape of a Pt particle deposited on a graphite substrate with that of a cubooctahedron with triangular (111) faces (fig. 1b).

Ino [6], using conventional bright and dark field transmission electron microscopy (TEM), observed that quite frequently small Au or Ag particles deposited on a cleaved crystal do not exhibit the uniform TEM contrast that would be expected for single crystalline particles. He suggested that these crystallites are composed of a number of smaller tetrahedral units of regular f.c.c. crystal structure. He described two types of so-called "multiply-twinned-particles" (MTP's), which are shown on fig. 1c and 1d. In this model the gap which would appear between the f.c.c. tetrahedra is compensated by a deformation of the crystalline lattice to allow their junction along the twin

(111) planes between two tetrahedra.

The stability of the MTP's compared to that of Curie-Wulff cubooctahedra with (111) hexagonal faces was calculated by Ino [7] using a thermodynamic approach. He calculated the total free energy of the cubooctahedron in summing the cohesive energy, the surface energy and the adhesive energy to the substrate; for a MTP particle he added the elastic strain energy and the twin boundary energy. He then assumed that both particles contain the same number of atoms and have the same volume (no lattice contraction) and calculated the difference in energy. He explained in this way the transition from cubooctahedron to icosahedron (ics) when the size decreases, by the lower surface energy of the (111) faces of ics, which more than compensates for the elastic distortion energy. The critical radius r_c found by Ino is given in table I for different f.c.c. metals, when the interaction with the support is neglected. We shall discuss later their relevance to the experimental data.

The existence of a critical radius does not mean that no MTP particles will be found for radii larger than r_c . On one hand, in most experimental situations the particles have not grown under equilibrium conditions, on the other hand, when the particles grow the internal strains become very large and it is not surprising that lattice defects which lower the energy appear. In recent work Schabes et al. [8] and L.D. Marks et al. [9] have observed dislocations in Au and Ag icosahedra larger than 150 Å in diameter. A geometrical model of the defects as well as a theoretical analysis of the strains have been proposed [10].

Yang et al. [11] have shown that the deformed tetrahedra in respectively the decahedron and the ics can be interpreted as regular lattice structure with a body-centered orthorhombic or rhombohedral crystal symmetry. They give experimental evidence [12,8], using high resolution electron microscopy and microdiffraction experiments, that the model based on f.c.c tetrahedral building units does not apply and in particular that there are no non-uniform lattice strains. These claims have been questioned by Marks and Smith [9,10] who conclude that the distortions in the ics are taken up by an inhomogeneous elastic strain in small clusters and by a combination of dislocations and inhomogeneous elastic strains in larger particles. Furthermore their microdiffraction data show that the structure of the tetrahedra is f.c.c.. These are certainly difficult experimental problems, as the differences could come from the different preparations of the samples and from their interaction with the underlying substrate. In particular it would be interesting to anneal the samples in order to reach the equilibrium shape of the aggregates.

C. Solliard [13] has made a detailed study of the shape and width of the diffraction peaks of Au and Pt samples evaporated and annealed on a carbon substrate, with average diameters ranging between 30 and 200 Å. He shows that for Pt the width Δ_{int} of the integrated diffraction peaks follows the usual "Scherrer straight line" $\Delta_{int} = 1.3/D$ where D is the average diameter of the samples. In comparing the width of the (220) and (440) peaks, which would be enlarged differently by non-uniform local deformation, he concludes that the average non-uniform strains in Pt are smaller than $2 \cdot 10^{-3}$.

In the case of Au MTP's the behavior is different, since the diffracting units are smaller than the particle itself. Furthermore he shows that for larger sizes ($D > 120$ Å) the width of the diffraction peaks does not decrease towards zero when D increases. The analysis indicates that it can neither be explained by a uniform deformation of the lattice, which would

give non observed structures in the shape of the diffraction line, nor by non-uniform deformations which are ruled out by the similar widths of the (220) and (440) diffraction peaks. The suggested explanation is that additional twin planes appearing in the particle reduce the diffracting units to dimensions smaller than those of the tetrahedra of a homothetically grown ics. This unfortunately does not give information for particles of diameter smaller than 120 Å.

The question still remains open if there are uniform or non-uniform deformations for metal MTP's of diameter smaller than about 100 Å. In the case of rare gas clusters, Farges et al. [1] have conclusively shown, both theoretically and experimentally, that the deformation in the MTP type structures are highly non uniform.

Recently Khanna et al. [14] have compared, for different sizes, the cohesive energy of cubooctahedral clusters with regular (111) triangular faces and icosahedral Pt clusters. This choice is convenient since it can be shown that both structures have the same number of atoms and that a small distortion of the cubooctahedron leads to the ics. The Moment method used, although it is not ab-initio and has simplifications (e.g. only the d electrons are taken into account), has given surprisingly good results for the elastic constants and has allowed to understand the evolution of the lattice parameters of transition metals as a function of band filling. We believe that it should be qualitatively accurate in predicting the stability of two geometrical structures which are obtained from one another by small distortion. The assumption of a uniform lattice has been made and the cohesive energy E_c is written as the sum of an attractive term E_B , corresponding to the electronic d band contribution, and a repulsive term E_R , described by a Born-Mayer potential between nearest neighbors. Both E_B and E_R depend on the geometrical structure of the clusters and on their interparticle distance R . For a given structure, the equilibrium values of E_c and R are obtained by minimizing E_c with respect to R . The relative stability of the cubooctahedron and the icosahedron is then determined by comparing their cohesive energy.

The evolution of the cohesive energy of the cubooctahedron and the ics as a function of the radius shows, as expected, that for small diameters ($D < 15$ Å) the ics is more stable than the cubooctahedron. A study of the asymptotic behavior for large diameters indicates that the difference between the bulk and the cubooctahedron cohesive energy decreases towards zero as $1/D$, while the difference for the ics cohesive energy decreases towards a constant value to which is also added a $1/D$ term. The constant value can be interpreted, following Ino's model, as the effect of the elastic distortion energy of the ics. It is closely related to the difference between the intra-shell R_t and inter-shell R_r interatomic distances ($R_r/R_t \approx 1.05$), which modifies the effective mean coordination number of the ics through its effect on the transfer integrals. The $1/D$ term is itself related to the surface energy and its stabilizing effect for the ics ($\gamma_{[111]} < \gamma_{[100]}$) is reflected in the smaller coefficient in front of the $1/D$ term for the ics than for that of the cubooctahedron. This model thus contains in the nearest neighbour approximation two of the contributions of Ino's model, but does not include, however, the twinning energies. It also predicts the contraction of the lattice parameters of Pt clusters as the size decreases. The agreement with the experimental data [13] obtained by electron diffraction on single crystalline Pt particles is good. The lattice contraction as a function of size has also been measured

for Au icosahedron [13], the electron diffraction results, however, only give an average value of the interatomic distances.

We have summarized in table I the information available on the occurrence of MTP type aggregates for the different f.c.c. metals. There are well defined cases. For example all experimental results show that Ag and Au easily form MTP's, while pentagonal clusters are seldom found for Pt, Pd and Al. In the case of Rh, the type of structures which have been found depends on the interaction with the support. Ni is a particular case. A detailed study has revealed that the particles have a decahedral shape with anisotropic growth. As already mentioned, in most cases no attempt was made to anneal the clusters in order to reach an equilibrium shape. The interactions with the substrate or adsorbed gases also certainly have an influence. The critical radius at which a transition is observed is thus not well known. It seems however that the values predicted by Ino's model are correct for Au and Ag and too large for Pd and Pt. Ino's values should however not be taken too strictly, particularly as they are based on bulk values for the anisotropic surface tensions and twinning energies which are not well known. Table I seems, however, to show that the metals whose twinning energies are low, easily form decahedra or ics.

It would certainly be useful, in order to clarify the situation, to take electron diffraction data on metal clusters in a beam. A promising attempt has been made by G. Stein and collaborators [15].

	Rh	Ni	Pd	Pt	Cu	Ag	Au	Al
r_c (Å)		22	25	28	34	38	53	15
twin boundary energy (erg/cm ²)		75	65	37.5	20	10.5	15	119
decahedra or ics	(yes) ^{a)}	(yes) ^{b)}	no	no	---	yes	yes	no
references	22,23	24	17,18,19 20	5,13,17 18,19,21		8,9,10,12,13,16,17		25,26

a) depends on the substrate b) decahedral shape with anisotropic growth

Table I : Summary of the occurrence of MTP crystal structures for f.c.c. metals. r_c is the critical radius calculated by Ino's model.

ELECTRONIC AND GEOMETRICAL STRUCTURE OF ALKALI METAL AGGREGATES

Metal aggregates can be produced in a beam either by supersonic expansion [27] or by a variation of the gas aggregation technique [28]. Alkali aggregates up to Nan ($n < 65$) [29,30,31], K_n ($n < 12$) [27] have been produced by these techniques and selectively identified by mass spectrometry. Small metal clusters can also be obtained by co-deposition of a rare gas and metal atoms on a cold substrate. The clusters are thus embedded in a frozen rare gas matrix, their temperature can be controlled easily, however it is more difficult to identify them with certainty. In the case of alkali metals, aggregates containing up to seven atoms have been identified [32].

Na and K are the metals for which the most extensive measurements of the ionization potentials (I.P.) are known. The appearance potentials have been measured up to Na_{14} [27] and K_8 [27]. As an example we give in figure 2 the measured values for Na clusters. Notice the oscillations which have been explained, using the Extended Hückel theory (EHT), by the odd and even number of electrons in the highest occupied molecular orbital. However, contrary to the prediction of the EHT, the odd-even character does not go beyond Na_8 . A detailed theoretical study of the electronic and geometrical properties of the

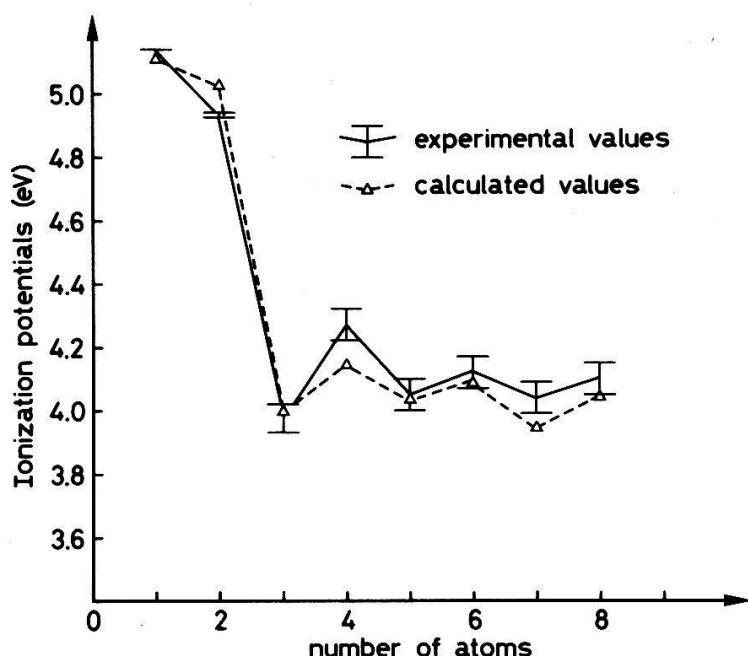


Figure 2 : Appearance potentials of Na clusters. The experimental values are taken from ref. 27 and the calculated values from ref. 34.

alkali clusters should include a treatment of electron correlation effects, since the binding and the correlation energies of the aggregates are of the same order of magnitude [33]. On figure 2 we have also reproduced the theoretical results of Flad et al. [34], they were obtained with a Hartree-Fock calculation in which correlation corrections were introduced with an "ad-hoc" local density scheme. To our knowledge this calculation is the only published computation which goes beyond clusters of 4 alkali atoms and which gives reliable informations on the cohesive energy, i.e. on the equilibrium geometrical structure of alkali clusters. The agreement between the calculated and measured IP is relatively good, but this agreement is not in itself a very crucial test of the geometrical structure, since aggregates of quite different shapes and of similar cohesive energy can have the same IP.

The two photon ionization spectra of Na_3 [30,35] and Na_4 [36], the laser induced atomic fluorescence spectra of Na_3 [37], the Rydberg states of Na_3 [38], have been studied in a beam, the optical spectra [39,40] of alkali clusters deposited in a frozen rare gas matrix are also known. However, the information provided by these experiments, which can in principle give precious information about the structure, is often difficult to interpret.

Raman measurements also would be very useful, and some work has been done in a matrix [41], but not for alkali clusters.

The magnetic properties of K_3 , Na_3 , Na_5 , Na_7 have been studied in a beam with a Stern-Gerlach apparatus [42]. They clearly show that the particles with an odd number of atoms have one unpaired spin, however informations concerning the structure of the clusters have not yet been obtained, due to problems related to the spin rotation interaction.

Up to now the most detailed information about the geometrical structure of alkali aggregates has been given by the electron spin resonance (ESR) measurements of Lindsay and collaborators. They have reported, as a function of temperature, the ESR spectra of Li, Na, K aggregates frozen in a rare gas matrix. These results show that at low temperature Na_3 [43] and K_3 [44] have a high and equal spin density ξ on two atoms ($\xi_{Na} = 0.47$, $\xi_K = 0.47$) and a small negative ξ value on the third one. At higher temperature ($T > 20$ K) another spectrum appears [45], which corresponds to trimers having an equal spin density on the three atoms. In the case of Li_3 [46], only this spectrum appears even at 4.2 K. They have also attributed to an aggregate formed of seven alkali atoms [32], a spectrum in which two atoms have the same high density ($\xi_{Li} = 0.27$, $\xi_{Na} = 0.37$, $\xi_K = 0.37$) and the remaining atoms have a small ξ value. These data can be used as a critical test of the geometrical structure of polyatomic alkali clusters as is shown below.

Recently a complete study of the Born-Oppenheimer surfaces of Li_3 , Na_3 and K_3 has been reported [33]. We used an approach based on the density functional theory, in which the pseudopotential approximation is chosen to describe the ionic cores and the local spin density approximation is used to treat the exchange and correlation effects of the valence electrons. This approach has the advantage of giving results for the ground state comparable in accuracy to the best configuration interaction (CI) calculations while allowing the treatment of clusters having more than two or three inequivalent atoms, which is the practical limitation of the CI methods. Recently J.L. Martins et al. [47] have shown that, within the pseudopotential scheme, it is possible with a reasonable basis set to use the Hellmann-Feynman forces in order to converge more quickly towards the equilibrium geometries of small clusters. This has been used, in a yet preliminary calculation, for a Na_7 cluster.

We give in fig. 3 the equipotential lines of the Born-Oppenheimer surface of Na_3 . Notice the three "obtuse" isosceles triangle minima (-1.02 eV) separated by the "acute" isosceles triangle saddle points (-0.99 eV) and the local minima (-0.96 eV) with a linear geometry. Notice also the higher energy of the equilateral triangle ($q_x = q_y = 0$), whose Jahn-Teller distortion gives rise to the two isosceles triangle minima. At low temperature the passage of one of the "obtuse" triangle minima to the two others can be made by tunneling through the potential barrier between two minima (height ≈ 0.03 eV = 350 K; tunneling frequency ≈ 1 MHz). In real space the passage from one minimum to the other corresponds to the passage of the "obtuse" angle from one apex of the triangle to the other. This can be obtained through a small displacement of the atoms, it is therefore called a pseudorotation.

On the basis of this model, when the relevant time scale of an experiment is smaller than the pseudorotation (or tunneling) time, the trimer appears as an "obtuse" triangle. That is the situation observed for the ESR spectra of Na_3 and K_3 at low temperature. At higher temperature, where

vibrational levels could be populated, the tunneling time shortens and on the average the experimental ESR spectrum looks like that of an equilateral triangle. This situation is always observed for Li_3 , and this is in agreement with our calculations (see also ref. 48) which indicate that the ground vibrational level is higher in energy than the essentially zero height of the barrier. Notice also that the measured spin densities are in agreement with those calculated for an "obtuse" isosceles triangle, but would be in disagreement with an "acute" triangle geometry. The ESR experiments, if we can neglect possible matrix effects, can thus probe not only the static but also the dynamic behavior of the alkali trimers on the Born-Oppenheimer surfaces.

Using the EHT, Thomson et al. [32] suggested that a pentagonal bipyramid (i.e. a decahedron) could explain their results for the septemer alkali clusters. Our preliminary density functional calculation, in which the two parameters of a regular pentagonal bipyramid were optimized, is in good agreement with the ESR results. A more detailed study should be made to see if it is the true equilibrium shape predicted by the theory.

On the basis of their calculation Flad et al. [34] suggested that Na_3 structures formed of Na_2 molecules could be more stable than compact structures. Although a more complete study should be done, our preliminary density of charge calculations indicate, on the contrary, that there are no directional bonds and that all atoms participate in the bonding.

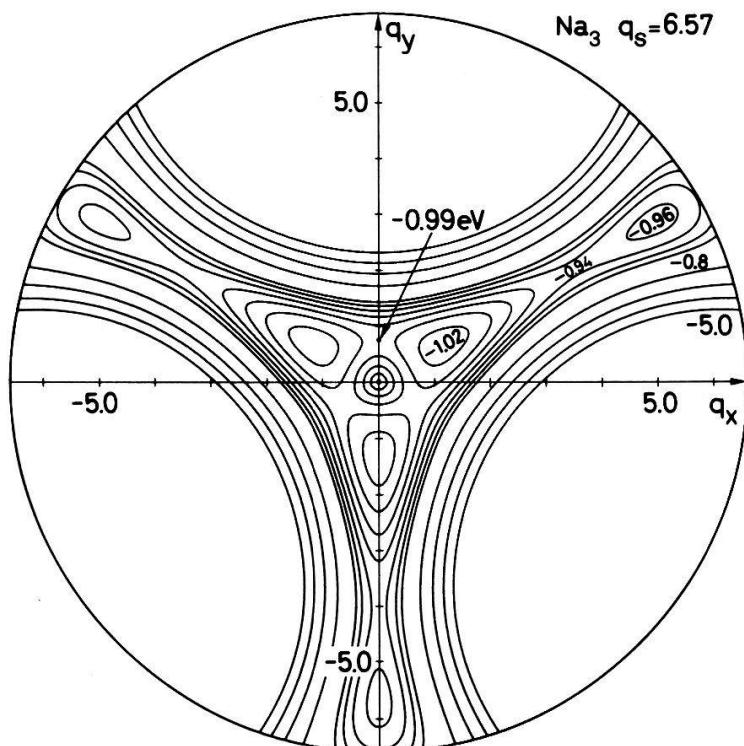


Figure 3 : Equipotential lines of the Born-Oppenheimer surface of Na_3 . The coordinates q_x , q_y , q_s are the normal coordinates of a triangle and the atomization energies are measured in eV.

CONCLUSION

Although a gap of knowledge exists between the very small clusters and the cluster with diameters larger than ~ 20 Å, the situation is not hopeless. Theoretical methods are now developing which will certainly help in bridging this gap, e.g. the binding energy and electronic structure of small Cu particles having up to 79 atoms have been studied [49]. The molecular beam techniques also are now able to produce clusters having more than 100 atoms [28] and a study of their structure using electron diffraction becomes feasible.

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