# Generation of Metal Clusters Containing from 2 to 500 Atoms

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The main problems underlying the experimental study of particles with sizes between single atoms and the solid state have been solved: the formation of metal clusters, their individual detection, and the separation of beams with uniform cluster size. By inert-gas condensation of metal vapors the clusters $Sb_1$–$Sb_{500}$, $Bi_1$–$Bi_{280}$, and $Pb_1$–$Pb_{400}$ have been produced. The high intensity observed over the whole mass range henceforth allows a systematic size-dependent investigation of metal clusters.

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The aim of metal-cluster physics is to get information about the physical properties of agglomerates in the size range between single atoms and the solid state. Formation mechanisms for small particles (more than a few hundred atoms per cluster) are known[1]; however, only broad size distributions could be achieved. This may be the reason why basic properties, like the quantum size effect,[2] could not definitely be confirmed by experiments.[3]

In the size range of metallic microclusters (less than a few hundred atoms per cluster) information is even scarcer because no satisfying preparation technique was available up to now, which allowed systematic investigations. Though clusters of metal atoms (Li,[4] Na,[5] K[5,6]) have been grown or sputtered,[9] these particles however contain only a small number of atoms (up to 16), and with increasing cluster size the intensity decreases by several orders of magnitude. Theoretical predictions of the most probable crystallographic structures,[8] the energy distribution of the electron states,[9] or even the stability of different cluster sizes depend strongly on the kind of theory, the choice of parameters like interatomic distances or the inclusion of refinements like electron-electron correlations.[10] In principle, the existence of metal clusters cannot be concluded from theoretical data and therefore was open to question so far.

We report on the first successful generation of metal clusters in the full size range between single atoms and small particles with direct evidence for the existence of the particles, which is obtained by mass spectroscopy. The unexpectedly high total intensity of the cluster beam, which is about 1000 times higher compared to the atomic beam without inert-gas condensation, the surprisingly weak decrease of the cluster intensity with increasing size, and the ability of separating particles of uniform mass by electronic time-of-flight (TOF) technique henceforth allow a systematic investigation of cluster properties.

The clusters are formed by nucleation from the metal vapor in a He-gas atmosphere enclosed in a liquid-nitrogen–cooled condensation cell (Fig. 1). They effuse from the cell by a little orifice ($O_1$, with diameter 1.5 mm), pass the differential-pumping section and enter the mass spectrometer (orifice $O_2$). The intensity of the neutral cluster beam is registered by a film thickness monitor. The TOF spectrometer is equipped with a synchronized electronic deflection system to separate single masses from the whole cluster spectrum. A detailed description of the apparatus is given elsewhere.[11]

In a preliminary experiment Sb vapor directly emitted from the surface (Langmuir evaporation) was analyzed. At $T = 800$ K antimony emits predominantly $Sb_4$ (intensity ratio $Sb_4$:$Sb_3$:$Sb_2$:$Sb_1$ = 77:6:8:9). Clusters with higher masses are not observed (less than $10^{-5}$ compared to the $Sb_4$ in-

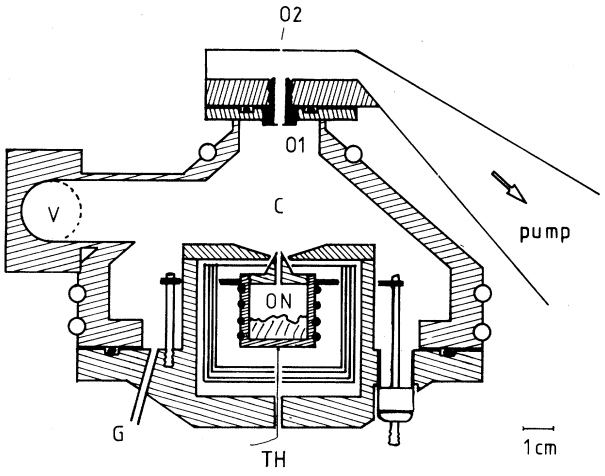


FIG. 1. Cluster source: ON, oven; C, condensation chamber; $O_1$, $O_2$, collimators; V, valve for vacuum connection; G, gas inlet; TH, thermocouple.

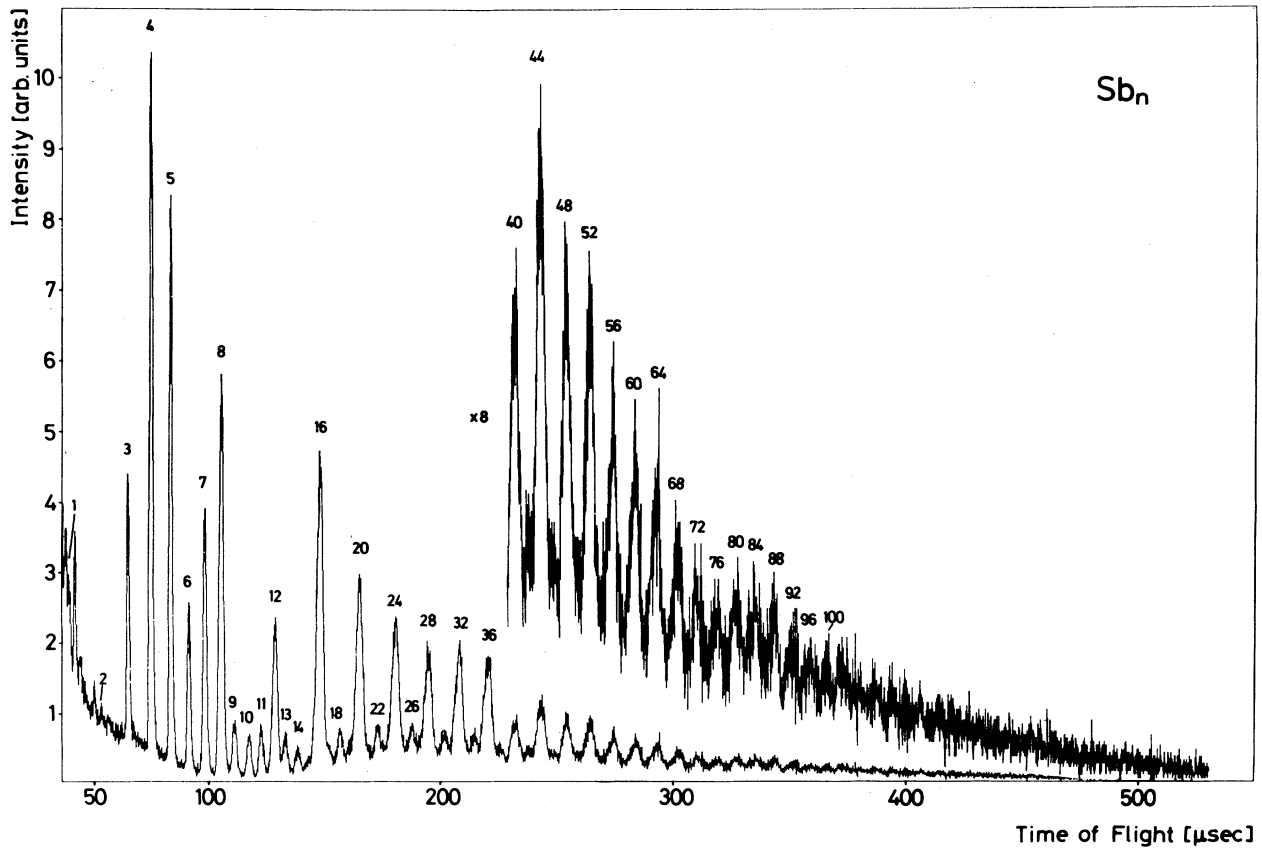


FIG. 2. TOF mass spectrum of antimony clusters, produced by condensation in He atmosphere. Only the resolved part of the spectrum is shown. Clusters have been detected up to 820 μsec.

tensity). As soon as He gas is added to the condensation cell (residual gas pressure $10^{-7}$ Torr), the intensity of the antimony beam decreases with increasing He pressure $p_{He}$ and gets zero at $p_{He} = 5 \times 10^{-1}$ Torr. Most probably the metal vapor is scattered in the He gas and is deposited on the walls of the condensation cell. Only after $p_{He}$ reaches 5 Torr, again an evaporation rate is registered at the film-thickness monitor. Simultaneously, a large number of Sb-cluster peaks appear in the TOF spectrum. At $p_{He} = 15$ Torr, the film thickness monitor shows an evaporation rate which is about three orders of magnitude higher compared to the rate without He gas added. We suppose that the clusters can only be extracted from the condensation cell if a suitable flow characteristics has been formed[12] immediately above the oven orifice, and that this flow characteristic also gives rise to the increase of the evaporation rate. We have found that microclusters cannot be formed if He is replaced by other noble gases and that even a small admixture of Ar or a slight temperature variation (~10%) of the He gas prevents their formation.

The TOF mass spectrum in Fig. 2 shows resolved clusters from $Sb_1$ to $Sb_{100}$ (12 000 amu). Up to $Sb_{16}$ every cluster mass appears in the spectrum followed by a sequence of $Sb_{4n}$ with smaller peaks of $Sb_{4n+2}$ in between. Above $Sb_{100}$ unresolved clusters up to $Sb_{500}$ (60 000 amu) are detected. The counting rate for a typical cluster like $Sb_{24}$ is 10 per second. This refers to a current of 100 μA of the nonpulsed electron source and a duty cycle of $2 \times 10^{-4}$. The broadening of the peaks with increasing cluster mass is due to the gradient of the electrostatic potential in the ionization zone of the ion lens.

In order to prove whether the conditions for Sb nucleation are generally applicable to metal cluster formation we have also investigated bismuth and lead. The TOF spectra are shown in Figs. 3 and 4, respectively.

Bi clusters have been observed up to $Bi_{280}$ (58 000 amu), with resolved cluster peaks up to $Bi_{21}$ (Fig. 3). The Bi spectrum does not show the tetramer sequence like for antimony. This is

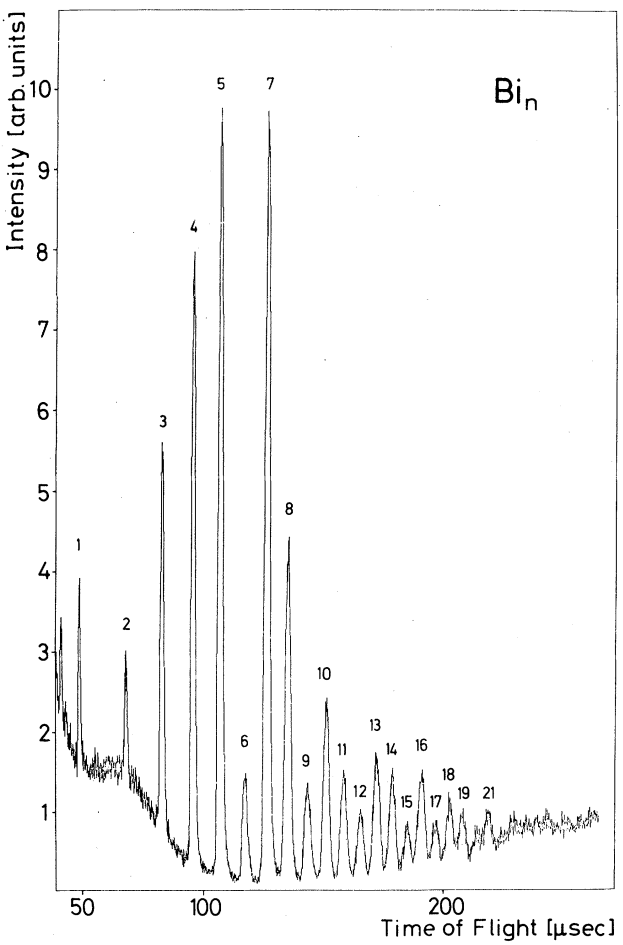


FIG. 3. TOF mass spectrum of bismuth clusters. The original spectrum ranges up to 800 μsec.

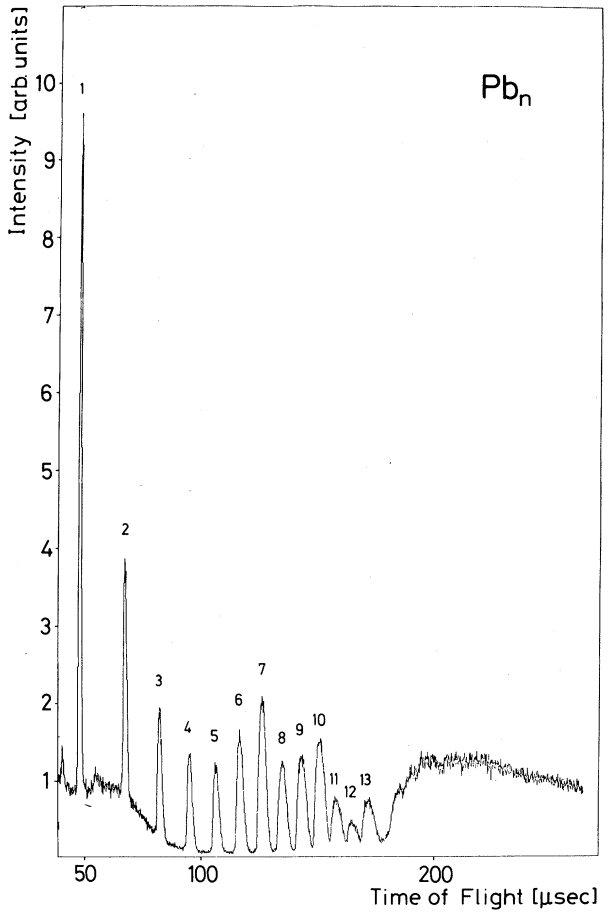


FIG. 4. TOF mass spectrum of lead clusters. The original spectrum ranges up to 950 μsec.

consistent with the probability for tetramer formation of the pnictides which is known to decrease from phosphorous to bismuth. The $Bi_n$ spectrum is characterized by increasing intensity up to $Bi_5$ and decreasing intensity for clusters larger than $Bi_7$. Rather low intensities are found for the sequence $Bi_6$, $Bi_9$, $Bi_{12}$, and $Bi_{15}$.

Figure 4 shows the TOF spectrum of lead clusters. The highest cluster masses observed are about $Pb_{400}$ (83 000 amu), while resolved clusters appear up to $Pb_{13}$. Between $Pb_3$ and $Pb_{13}$ the cluster $Pb_7$ occurs with the highest intensity.

In the case of small particles, the supersaturation obtained by inert-gas condensation is assumed to be so high that growth occurs by coalescence of clusters rather than by successive nucleation, and a statistic theory which involves only the coalescence process but not information about element specific cluster properties describes the shape of the size distribution.[1]

We find for antimony a weak decrease of the cluster density with increasing mass: related to $Sb_4$, e.g., $I(Sb_{16}) = 84\%$, $I(Sb_{32}) = 32\%$, and $I(Sb_{64}) = 9\%$. In the case of bismuth, the clusters $Bi_5$ and $Bi_7$ appear with even higher intensities than the "parent particles" $Bi_1$ and $Bi_2$. Thus we conclude, that coalescence cannot be neglected in a growth mechanism of microclusters, so that theories based upon successive nucleation[13] are not applicable.

The characteristics of the cluster spectra $Sb_n$, $Bi_n$, and $Pb_n$ are different for $n \lesssim 20$, indicating that in this range the size distribution cannot be explained by a growth statistic alone, but depends also on the stability of the clusters. In a first approximation, the ionization cross section as well as the detector efficiency can be regarded to be constant for neighbored clusters. Thus, the lower abundance of $Bi_6$, $Bi_9$, $Bi_{12}$, and $Bi_{15}$ might be caused by weaker binding energies of

these clusters. For $n \gtrsim 20$ the mass distribution strongly depends on the formation conditions and is mainly determined by the growth statistics. This is confirmed by the fact that the high-mass end of the distribution shifts to smaller masses with decreasing evaporation temperature but leaving the relative intensities for $n \lesssim 20$ nearly unchanged.

In summary, the essential preconditions necessary for systematic investigations of physical properties of particles in the size range between single atoms and the solid state is fulfilled, namely the production of metal clusters, their individual detection and the separation of beams with uniform cluster size. Thus, besides a further detailed investigation of the production process, the development of the collective phenomena, characteristic for the solid, can be studied as a function of particle size.

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[1]C. G. Granqvist and R. A. Buhrmann, J. Appl. Phys. 47, 2200 (1976).

[2]H. Fröhlich, Physica (Utrecht) 4, 406 (1937); R. Kubo, J. Phys. Soc. Jpn. 17, 975 (1962); L. P. Gor'kov and G. M. Eliasberg, Zh. Eksp. Teor. Fiz. 48, 1407 (1965) [Sov. Phys. JETP 21, 940 (1965)].

[3]F. Meier and P. Wyder, Phys. Rev. Lett. 30, 181 (1973); P. Yee and W. D. Knight, Phys. Rev. B 11, 3261 (1975); C. G. Granqvist, R. A. Buhrmann, J. Wyns, and A. J. Siervers, Phys. Rev. Lett. 37, 625 (1976).

[4]K. Kimoto and I. Nishida, J. Phys. Soc. Jpn. 42, 2071 (1977).

[5]A. Herrmann, S. Leutwyler, E. Schumacher, and L. Wöste, Helv. Chim. Acta 61, 453 (1978).

[6]W. D. Knight, R. Monot, E. R. Dietz, and A. R. George, Phys. Rev. Lett. 40, 1324 (1978).

[7]M. Leleuter and P. Joyes, Radiat. Eff. 18, 105 (1973).

[8]W. Romanowski, Surf. Sci. 18, 373 (1969); M. R. Hoare and P. Pal, Adv. Phys. 24, 645 (1975).

[9]J. Smith and J. G. Gay, Phys. Rev. B 12, 4238 (1975); R. P. Messner, S. K. Knudson, K. H. Johnson, J. B. Diamond, and C. Y. Yang, Phys. Rev. B 13, 1396 (1976); R. O. Jones, P. J. Jennings, and G. S. Painter, Surf. Sci. 53, 409 (1975).

[10]M. Torrini and E. Zanazzi, J. Phys. C 9, 63 (1976).

[11]K. Sattler, J. Mühlbach, A. Reyes Flotte, and E. Recknagel, to be published.

[12]Flow characteristics in the condensation region have been observed by light scattering on small particles: S. Kasukabe, S. Yatsuga, and R. Uyeda, Jpn. J. Appl. Phys. 13, 1714 (1974).

[13]R. Becker and W. Döring, Ann. Phys. (Leipzig) 24, 719 (1935); F. Kuhrt, Z. Phys. 131, 185 (1952); J. Feder, K. C. Russel, L. Lothe, and P. M. Pound, Adv. Phys. 15, 111 (1966); D. Kashchiev, Surf. Sci. 18, 389 (1969); K. Binder and D. Stauffer, Adv. Phys. 25, 343 (1976).

# Adatom Configurations of H(2×6) and H(2×1) on Ni(110) Analyzed Using He Diffraction

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The first determination of *two-dimensional* adsorbate-induced corrugation functions from He-diffraction data is reported. Local maxima in the corrugations of both H(2×6) and H(2×1) on Ni(110) directly reflect adatom positions due to the localized charge distribution of the chemisorbed H atoms. Hence, genuine information on the adsorption sites is obtained leading to novel insight into coverage and adsorbate-adsorbate interactions. The transition to the reconstructed (1×2) saturation phase is discussed.

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Although H adsorption on metal surfaces is of high current interest both theoretically (e.g., chemisorption-model system)[1,2] and for technical reasons (surface chemistry, H uptake in metals),[3] only one low-energy electron-diffraction (LEED) study concerning the surface location of H has been published.[4] LEED is of limited use here as H atoms scatter electrons very weakly, and additional diffraction features are extremely faint unless the H adsorption is accompanied by a reconstruction of the substrate.[5,6] On the other hand, the corrugation function obtained from He diffraction is a replica of the surface charge density,[7] and undergoes severe changes upon adsorption of any substance.[8] In our previous He-diffraction study of H(1×2) on Ni(110),[9] the surface structure remained unsolved, as several models were consistent with the one-dimensional corrugation ob-