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Disperse Condensates of Metal Vapour

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This review deals with the role of associated complexes in the condensation and crystallisation of metals from their vapours. The presence in the metal vapour of polyatomic complexes (whether originally present or formed above the evaporation surface) is shown to have a significant influence on the initial condensation step on a solid surface or in an inert carrier gas. The mechanism of formation of highly disperse aerosol metal particles is discussed in detail. Some aspects of crystal and film growth from the vapour are briefly mentioned. 288 references.

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1. INTRODUCTION

Metal vapours are usually treated as monatomic ideal gases in studies of elementary crystallisation processes from the gas phase (preparation of aerosol particles, and growth of single crystals, whiskers, and films).

The possibility of formation of polyatomic complexes in the gas phase is often ignored. Yet, complexes of this type can be evolved during evaporation of a metal, or alternatively they can be formed by atomic collisions if conditions are favourable to the removal of the heat of condensation.

Since the condensation of a metallic vapour is essentially a non-equilibrium process, it is important to define the kinetic aspects of the irreversible dissipation of the energy of the colliding atoms. In principle, this energy can be dissipated by ternary collisions of the metal atoms close to the evaporation surface, or by ternary collisions involving atoms of the carrier gas, the excess of energy being eventually transferred to the walls of the vessel.

In an analysis of the elementary processes involved in the crystallisation of a metal from its vapour, it is important to include the irreversible dissipation of the energy of the condensing atoms and the subsequent growth and coagulation of the polyatomic complexes. This approach is gaining wide acceptance.

2. POLYATOMIC COMPLEXES IN REAL GASES

Many scientists (Boltzmann, Clausius, van der Waals, and others) have ascribed departures from ideal gas behaviour to the formation of associated complexes in real gases[1].

Much experimental evidence (both direct and indirect) is now available on the existence of these associated species in the vapour of practically all substances. Most of the work has concentrated on measurements of the partial pressure and dissociation energy of dimers. The results have been summarised in a number of reviews[2-6].

The analytical methods most commonly used to study the composition of the gas phase are the spectroscopic[2,3] and the mass spectrometric method[4], but other methods also have been applied: measurements of molecular velocities, measurements of the displacement of a molecular beam in a magnetic field, the magnetic resonance method, the torsional variant of the effusion method, and the beam density method.[5]

The dissociation energy of the dimer is usually referred to a temperature of 0°K, and is denoted by D_0.

D_0 values for approximately 40 elements up to Rn ($Z = 86$) are known at present. However, among the 23 transition metals the bond energy of the dimer is known only for nickel ($D_0 = 3.36 \pm 0.217$ eV).[7]

Drowart and Honig[4] showed that D_0 varies periodically with the atomic number Z. Verhaegen and coworkers[6] established a periodic dependence upon the atomic number Z of the ratio of the heat of evaporation of an atom at 0°K (ΔH_0) to the dissociation energy of the dimer D_0. All the existing data fall into three distinct classes, depending on the electronic structure of the element.

The relative equilibrium vapour pressure of the dimer (P_2) is given by the expression[6]

$$\frac{P_2}{P} = \text{const}\, e^{\frac{\Delta H_0}{RT}\left(\frac{1-\alpha}{\alpha}\right)},$$

where P is the vapour pressure of the monomer, R is the gas constant, T is the absolute temperature, and $\alpha = \Delta H_0/D_0$. If $\alpha < 1$, the concentration of the dimer decreases with increase of temperature. This is the case with molecules which are known to be stable at low temperatures (N_2, I_2, etc). For Bi_2, $\alpha \simeq 1$, and we can expect the relative amount of the dimer to be insensitive to temperature. Experimentally, the proportion of Bi_2 in the vapour shows a fast initial increase with temperature, reaches a maximum of ~45% in the region of 500°, and then begins to decrease slowly.[8] More recent measurements, however, suggest that the concentration of dimers may remain constant in the region 500–900°, since a vapour composition of 43% Bi + 57% Bi_2 has been reported[9] for 900°.

When $\alpha > 1$, as in the case of carbon and the metals, the proportion of dimers in the saturated vapour increases with temperature. Thus, for sodium vapour $P_2/P = 8.61 \times 10^{-4}$ at 127° and 0.25 at 727°; similar (though numerically smaller) values are obtained for Li and K vapours[5].

For Cu, Ag, and Au, $\alpha = 1.8 \pm 0.1$,[6] and the relative concentration of dimers in the temperature region 1300–1500°K is $(4-10) \times 10^{-4}$.[10] Other examples can be found in Nesmeyanov's monograph[5].

The vapours of some alloys (Ag–Au, Ag–Cu, Au–Cu,[11] and Ag–Sn, Au–Sn, Cu–Sn[12]) contain, in addition to atoms of the components, also symmetrical (Cu_2, Ag_2, Au_2, Sn_2)

and unsymmetrical dimers (AgAu, AgCu, AgSn, AuSn, AuCu, CuSn). The bond energies of these dimers are listed in Table 1.

These values are comparable to the dissociation energies of molecules such as Cl_2, Br_2, I_2.

Table 1. Bond energies of some metal dimers

Dimer	T, °K	D, eV	Literature reference	Dimer	T, °K	D, eV	Literature reference
Ag_2	1260—1360	1.63±0.03	10	AgAu	0	2.06±0.096	11
		1.9±0.3		AgCu	0	1.77±0.096	11
	0	1.78±0.10	13	AuCu	0	2.36±0.096	11
	0	1.63±0.096	11	AgSn	0	1.37±0.217	12
Au_2	1500—1610	2.18±0.03	10	AuSn	0	2.5±0.174	12
		2.3±0.3		CuSn	0	1.8±0.174	12
	0	2.30±0.12	13		1440—1560	2.02±0.03	10
	0	2.24±0.096	11			2.1±0.3	
Sn_2	0	1.99±0.174	13	Cu_2	0	2.21±0.11	13
					0	1.97±0.096	11

The bond energy D of the dimer can be simply related, in the case of hydrogen-like atoms, to the ratio of the ionisation potentials[14] of the given atom and of the hydrogen atom:

$$D = \frac{e^2}{4r_0}\left(\frac{I_X}{I_H}\right)^{1/2},$$

where e is the electronic charge (c.g.s.) and r_0 is the equilibrium separation of the atoms in the dimer. The extent to which this formula applies in practice is evident from Table 2.

Polyatomic complexes have been found to exist in many vapours. Thus, Miescher and Metzger[15-17] made the following observations in their study of the molecular complexity of vapours. Tellurium evaporates as Te_2 at 320°, selenium evaporates as 90% Se_6 and 10% Se_2 at 180°; arsenic evaporates as As_4 at low temperatures, as 70% As_2 + 30% As at 260°, and the vapour consists almost exclusively of As_4 molecules up to 530°.

According to Niwa and Yosiyama[18], selenium evaporates as an equilibrium mixture of Se_6 and Se_2, the proportion of Se_2 increasing from 12% at 185° to 25% at the boiling point. The presence of Se_2, Se_6, and Se_8 in selenium vapour near the boiling point has been inferred from measurements of the vapour density[19,20].

Early measurements[5] indicated that the vapour over liquid antimony consists of molecules containing 1, 2, and 4 atoms, whereas on approaching the boiling point the vapour consists mostly of dimers.

These results have been confirmed more recently by a mass spectrometric method[21], and some interesting features of the evaporation of antimony (both pure and from Au–Sb alloys) have been pointed out. Antimony vapour at ~550° consists entirely of Sb_4, whereas the vapour over an Sb–Au alloy contains Sb_2 and Sb in addition to Sb_4; at 950° the vapour contains 10% Sb and 25% Sb_2. On increasing the temperature from 800 to 1100° the concentration of Sb_2 and Sb increases by a few per cent because the concentration of Sb_4 decreases. The composition of the vapour is independent of the concentration of antimony in the alloy between 15 and 60%.

Searcy and coworkers[22], using the torsional variant of the effusion method, detected a large concentration of polyatomic molecules in silver vapour at pressures of 10^{-6}–10^{-4} atm. In the temperature range 1310–1420°K the effective molecular weight of the vapour was $M = 278 \pm 90$, corresponding to a molecular complexity of 2.56. The lack of agreement with Drowart and Honig's mass spectroscopic results[10] is probably due to a significant concentration of polyatomic complexes which escaped detection by the mass spectrometer. Korniev and Vintaikin[23] studied the sublimation of silver by combined radiochemical and mass spectrometric methods, and showed that (in contrast to evaporation from the melt[22]) evaporation from the solid involves exclusively monatomic species. Positive and negative polyatomic ions were detected in the mass spectra of Se, Te, Sb, and Bi vapours[24]. Mass spectrometric studies[25] of Ge, Sn, and Pb vapours revealed polyatomic complexes up to mass number ~400 at pressures of 5×10^{-6}–5×10^{-4} mmHg. The published plots make it clear that the predominant polymeric species in Ge vapour consists of 4-atomic groupings, whose proportion at 1300 and 1370° is 7×10^{-3} and 2×10^{-2} respectively of the number of single atoms.

Table 2. Dissociation energies of the dimers of some elements[14]

Dimer	$(I_X/I_H)^{1/2}$	r_0, Å	D, eV (observed)	D, eV (calc.)	Dimer	$(I_X/I_H)^{1/2}$	r_0, Å	D, eV (observed)	D, eV (calc.)
H_2	1.000	0.74	4.75	4.85	Sb_2	1.928	2.22	3.0—3.72	3.28
Li_2	0.630	2.67	1.05—1.14	0.85	Bi_2	1.966	2.38	1.72—3.62	2.97
Na_2	0.615	3.08	0.74	0.72	O_2	1.896	1.21	5.21	5.64
K_2	0.566	3.92	0.52	0.52	S_2	1.577	1.89	3.4—4.4	3.00
Rb_2	0.554	4.22	0.49	0.47	Se_2	1.505	2.16	2.37—3.55	2.52
Cs_2	0.536	4.57	0.45	0.42	Te_2	1.435	2.59	2.32—3.18	1.99
C_2	1.629	1.31	3.60—4.95	4.46	F_2	1.134	1.43	1.6—2.8	2.85
N_2	2.577	1.09	7.51—9.90	8.46	Cl_2	0.974	1.99	2.51	1.76
P_2	2.182	1.89	4.14—5.08	4.14	Br_2	0.931	2.28	1.99	1.47
As_2	2.071	1.91	3.99	3.90	I_2	0.876	2.67	1.56	1.18

In tin vapour the ions Sn_2^+ and Sn_4^+ were detected at < 1% concentration at 1200°; the ratio of ion currents for the evaporation of lead (~800°K) was $Pb_2^+/Pb^+ = 3 \times 10^{-5}$. Schissel[13] found a significant concentration of trimers and tetramers in Cu, Ag, and Au vapours.

Carbon vapour gives a large number of peaks in the mass spectrum[4,26,27], from which the partial pressures of C, C_2, C_3, ..., C_7 molecules have been computed up to 4000°K.[28] A large number of polymeric molecules was found in the mass spectra of C, Be, Mg, Ti, Fe, and Cu vapours generated in a high-frequency discharge[29]. Under these conditions, molecular ions up to C_{31}^+, Be_{25}^+, Al_{14}^+, Mg_5^+, Ti_5^+, Fe_6^+, and Cu_5^+ can be detected.

The dissociation energy of the complexes Bi_2, Bi_3, Bi_4, and BiPb has recently been determined mass spectrometrically[30].

Most workers are of the opinion that the polyatomic complexes appear in the mass spectrum as a result of the evaporation of organised groupings from the liquid metal. This opinion is based on the low probability of binary and ternary atomic collisions at low pressures of metal vapour (10^{-4}–10^{-5} mmHg) over a crucible or in a beam emerging from a Knudsen cell, and also on the pressure independence of the various ion current ratios[24,25]. Martynkevich[31,32] has stressed the correlation between the complexity of the vapour and the structure of the liquid metal. These views are confirmed by the effect of irradiation with thermal neutrons on the composition of indium vapour[33]: after

irradiation, the ratio of ion currents for dimers and monomers in the temperature range 773–1373°K increases by a factor of 15–50. The effect of irradiation persists for a long time (up to one year), but falls off rapidly if the sample is heated 50–100° above the working temperature.

Studies[34-40] of the mass spectra of gases escaping at supersonic speeds into a vacuum from an orifice are very relevant to the mechanism of formation of polyatomic complexes. Associations of ten or more molecules have been detected in molecular beams of many gases (Ne, Ar, N_2, O_2, CO_2, H_2O, NH_3, N_2O, C_2H_6, C_3H_6), and the complexes $ArCO_2$, Ar_2CO_2, $Ar(CO_2)_2$, etc. have been identified in molecular beams of CO_2–Ar mixtures. It is assumed that these associations must be present at equilibrium in the reservoir[34], or alternatively they must be formed during the adiabatic expansion of the gas[35,37-39]. On changing the pressure in the reservoir from 100 to 700 mmHg the mean number of molecules in N_2 associations increases from 160 to 6500, and the proportion of free molecules in the beam falls from 30 to 0.15%.[40]

These experimental findings indicate the presence of large numbers of polyatomic complexes in real gases. As a rule, these complexes do not generate a large partial pressure, they cannot contribute significantly to the observed pressure dependence of the low-temperature thermal conductivity and viscosity coefficients[41], and they have no effect on the formation of films on solid surfaces. The presence of molecular associations in moist air manifests itself in the absorption of ultrasonic energy[42]. Hence, no theory of gases can be satisfactory unless it makes allowance for the presence of associated complexes.

Mayer's group theory[43,44] was the first step towards a solution of this problem. This theory, based on the approximate evaluation of the partition function, treated a real gas as a rapidly changing assembly of non-interacting groups of 1, 2, 3... molecules.

Band[45], Frenkel'[46,47], and Vukalovich and Novikov[48,49] produced independently—and almost simultaneously—an approximate formulation of the complete functional dependence of the molecular weight distribution of the complexes upon pressure and temperature. Their theories rely on similar physical assumptions, which were most clearly stated by Vukalovich and Novikov as follows:

1. Molecular association is a basic process common to all states of a gas.

2. Association is caused by the van der Waals interactions between gas molecules. Because these forces are weaker than the chemical bonds holding simple molecules together, the latter retain their structure and their properties in the complex.

3. Complex formation occurs by the collision of at least three molecules; some of the colliding molecules combine into relatively stable aggregates, whilst the remainder take away the heat of condensation in the form of translational kinetic energy.

4. The associated complexes are assumed to be in thermodynamic equilibrium with the single molecules and to have the same translational energy. The average life-time of the complex is much greater than the duration of a simple molecular collision. Below the critical temperature of the liquid–vapour phase transformation the bond energy of the association is higher than the thermal energy, and the dimers are stable. As the size of the complex increases, the bond energy of each molecule within the complex also increases. As Tables 1 and 2 show, the bond energy of the dimers can be much higher than the thermal energy.

5. A real gas is treated as a mixture of simple gases, consisting of single molecules, dimers, trimers, etc. When the system is in equilibrium, the dissociation of the complexes in any of these gases is exactly compensated by the formation of the same complexes from the simpler species present in the other gases. These processes are entirely analogous to reversible chemical reactions.

Frenkel'[46,47] developed the theory of hetero-phase fluctuations, according to which the distribution of associated complexes is described by the general formula of fluctuation probabilities:

$$N_r \sim \text{const}\, e^{-\Delta\Phi(r)/kT},$$

where N_r is the number of complexes having radius r, and $\Delta\Phi(r)$ is the fluctuation in the thermodynamic potential of the gas resulting from the appearance of a complex with radius r. The calculation predicts a substantial proportion of aggregates containing upwards of 1000 molecules in the saturated vapour.

Ginnel[50] developed a theory of association from the concepts of chemical kinetics. Taking account of topological differences between complexes (linear and closed chains) he deduced a system of equations from which equilibrium constants for the growth and decomposition of the aggregates could be obtained by the matrix method.

Chakraverty[51] discussed the formation kinetics and the steady-state distribution of complexes over molecular weight by solving the stochastic problem.

The concentration of dimers in Ar, Kr, etc. at ordinary temperatures and pressures was found[52] to be approximately 0.1% by an approximate evaluation of the statistical integral.

Since the presence of associated complexes in any real gas is now experimentally established, it becomes imperative to re-examine the problem of liquid–vapour phase transformations.

We are not concerned here with a discussion of the classical theory of the condensation of a supersaturated vapour developed by Volmer and Weber[53] and by Becker and Döring[54] (VWBD), based on the concept of a critical nucleus arising in an ideal monoatomic vapour at some well defined critical supersaturation as a result of fluctuations. The many theoretical and experimental studies of this problem have been adequately summarised in review articles and monographs[55-60]. We shall confine ourselves to a few remarks.

The VWBD theory is unsatisfactory in that it attempts to apply Kelvin's equation to very small aggregates: the concept of surface free energy becomes meaningless when most of the atoms lie on the surface[61-63]. Studies of the thermodynamics of very small systems are continuing to attract attention[64-71].

Attempts have been made[72,73] to deal with polyatomic complexes within the framework of the VWBD theory. The kinetic equations[54] were generalised by including the attachment or removal of complexes as well as single atoms. Frisch and Willis[72] found that the probability of formation of critical nuclei in the vapour is increased by the presence of dimers. However, Katz and coworkers[73] reached the opposite conclusion. Dunning[74] found an analogy between Mayer's and VWBD's theories under certain conditions.

In any nucleation theory based on Mayer's approach, the Mayer groups must be indistinguishable from the real polyatomic complexes found in the supersaturated vapour. If the Brownian motion (both rotational and translational) of the droplets is ignored, this approach leads to an equation for the equilibrium concentration of critical nuclei which is identical to the corresponding equation in the VWBD theory[75].

According to Lothe and Pound[76], allowance for the translational and rotational motion of the polyatomic complexes increases the classical rate of homogeneous nucleation by a factor of 10^{17} (!). A lively polemic on this topic is in progress[77-83].

The VWBD theory fails to take account of the influence of an inert carrier gas. As Bradley points out[84], the theory is not applicable at high pressures, because the diffusion parameters (which play an essential role under these conditions) do not appear in the formula for the rate of formation of critical nuclei. Bradley shows by a thermodynamic argument that on increasing the pressure of inert gas the supersaturated vapour becomes undersaturated, and the rate of formation of critical nuclei falls to zero.

In the presence of equilibrium polyatomic complexes in the vapour phase we are compelled to re-examine critically both the concept of a vapour phase and the familiar concept of "supersaturation", which has hitherto been applied exclusively to a non-associated vapour. The problem is to define the maximum size of a complex which can be treated as part of the gas phase from the point of view of partial pressure, density, and therefore also degree of supersaturation.

On the other hand, it is not easy to define the size of complexes beyond which one must treat the phase as condensed.

On changing the pressure or the temperature of a vapour, the complexes adopt a new size distribution, and a macroscopic liquid is simply the largest drop within the given distribution of complexes. From this point of view, the concept of supersaturation has no clear meaning, since a pressure in excess of the equilibrium pressure of non-associated vapour does not give rise to a distinct new phase but simply alters the size distribution of complexes in the vapour.

It is important to stress the fact that all the statistical and thermodynamic theories of vapour condensation discussed above rely on equilibrium (reversible) models. Yet, the condensation of a vapour is essentially a non-equilibrium, irreversible process, governed largely by the problem of dissipating the energy of the colliding atoms.

In the presence of an inert gas or of solid surfaces, which can disperse the heat of formation of the polyatomic complexes, both the steady-state size distribution of the complexes and the overall process of homogeneous condensation may be profoundly affected.

The problems arising from the irreversibility of the condensation of metal vapour are further complicated by diffusion and convective currents in the carrier gas, and by the relatively large temperature gradients in the vicinity of the evaporation surface.

3. CONDENSATION OF METAL VAPOURS IN AN INERT GAS

Many experimental studies of the formation of aerosol particles from metal vapours in the presence of an inert gas have been published. The earliest attempt to formulate the quantitative aspects of the problem was made in 1912 by Kohlschütter and coworkers[85,86]. Volatile metals (Zn, Cd, Se, As) were slowly distilled in a vacuum or under various pressures of different gases (H_2, N_2, CO_2). The size and density of condensate particles formed on a known area of glass or quartz were studied under an optical microscope (56–300 × magnification). No significant differences were observed on varying the rate of evaporation or the position of the substrate. All the particles were approximately spherical; spherulites and dendritic crystals were occasionally found in the selenium condensates. The main conclusions of this work were:

1. As the gas pressure increases from 55 to 850 mmHg, the particle size decreases from ~0.1 to ~0.001 mm.

2. For equal pressures, the size of the particles and the density of the deposit depend on the nature of the gas. The average particle diameter decreases from H_2 to N_2 to CO_2.

3. In hydrogen the deposits are denser than in CO_2; mirror-like deposits are obtained in a vacuum and at very low gas pressures, and at atmospheric pressure the deposits are powdery, with large inter-particle separations.

These results have been treated in various monographs[87-89] as giving a true picture of the formation of aerosol particles. However, it is now obvious that only the large secondary conglomerations were detected in Kohlschütter's experiments. More recent (see below) electron-microscopic work reveals an entirely different picture of the relationship between the pressure and nature of the background gas and the disperseness of the primary aerosol particles.

Gen and coworkers[90] studied the condensation of sodium vapour in the presence of xylene and butadiene vapours. They developed an industrial method of production of organosols by high-frequency heating of the sodium directly within the liquid. The preparation of metallic sols by striking an electric arc in a liquid (proposed by Tikhomirov and Lidov[91] and realised by Bredig[92] and Svedberg[87]) is obviously another instance of the condensation of a metal vapour in the presence of the vapour of a liquid.

Aerosol particles of metals and oxides have been studied in the electron microscope for many years[93,94], and the first attempt to correlate the size of particles with the conditions under which the particles had been formed was made in 1948.[95] Gold was evaporated from a heated tungsten wire, in a nitrogen atmosphere, and the deposits were studied on a collodion film. For a constant rate of evaporation (3 mg s^{-1}), the smallest spherical particles (15–100 Å, average diameter ~40 Å) were obtained at a pressure of 0.3 mmHg, whereas at 1–3 mmHg pressure the particle size was 125–200 Å. On increasing the rate of evaporation from 0.5 to 15 mg s^{-1} (N_2 pressure 0.5 mmHg) the amount of material deposited increased very considerably but the mean particle diameter was unaffected. Small additions of oxygen to the nitrogen (1.32 mmHg N_2 + 0.08 mmHg O_2) had no effect on the electron diffraction patterns. However, the topographic structure of the deposit was altered, and the transmission of infrared radiation increased. This effect is ascribed[95] to condensation of the volatile tungsten oxide WO_3. A highly disperse gold deposit has been shown[96] to be an efficient absorber of infrared radiation, with very little reflection.

During the 1930's, Pfund had reported[97-99] that black condensates of Bi and Zn are obtained in an inert gas atmosphere or in a moderate vacuum. Levinstein[100] showed that the phenomenon is a universal one, and ascribed it to the formation of aerosol particles during condensation of a metal vapour in the presence of background gases. He showed that the appearance of the metal condensate on a collodion film under the electron microscope undergoes profound changes as the residual gas pressure is increased from 10^{-5} to 0.1 mmHg during evaporation. The deposits obtained under high vacuum conditions (~10^{-5} mmHg) consist of separate crystallites with a well defined shape (in the case of Zn, hexagonal platelets ~10^{-5} cm in

diameter), but on raising the pressure to 0.1 mmHg most metal condensates present a uniform appearance (a black film consisting of a large number of particles ~10^{-6} cm in diameter). The most unexpected result was obtained in the evaporation of Zn and Cd at the relatively high pressure of 0.01 mmHg: the resulting condensates had a surprisingly uniform structure and a specular surface. Levinstein explains these phenomena by pointing out that the metal vapour in the presence of residual gas is not atomic, but consists of a cloud of particles which are probably formed near the evaporation surface. When these particles land on the target they remain indefinitely on their adsorption sites and act as condensation centres. On the other hand, the adsorbed atoms can re-evaporate from the surface until they are eventually captured. Metal deposits (Au, Ag, Cu, Ni, Fe, Co, Cr, Mn, Ti, Be, Pb, Sn, Pd, Pt) give sharp electron diffraction lines when condensed in a high vacuum. On the other hand, condensates of those same metals obtained at a pressure of 0.1 mmHg give diffuse rings. The electron diffraction patterns of W, Ta, Ir, Nb, Rh, Ge, and Si show diffuse rings irrespectively of vacuum conditions during depositions. Levinstein concludes that the particles formed near the evaporation surface are essentially indistinguishable from the crystallites obtained on the surface of the substrate when a high-melting metal is evaporated (W, etc.), but the crystallinity of the former is less developed than that of the latter when the metal is low-melting (Au, etc.).

Bagguley[101] prepared aerosol particles of Ni, Co, and Fe, and of Fe–Si, Fe–Cr, and Fe–Ni alloys by striking a high-frequency arc between electrodes of the experimental material in a hydrogen atmosphere. Suspensions of these particles in paraffin oil were used in studies of ferromagnetic resonance.

Sheftal' and coworkers[102,103] showed that the films of Ge and Si deposited on single crystals of the same materials in a hydrogen atmosphere (760 mmHg) had better structural and electrical properties than the films obtained in a vacuum. This phenomenon, analogous to the formation of mirror-like deposits of Cd and Zn in Levinstein's experiments[100], is explained by postulating the deposition of Ge and Si aggregates from the hydrogen gas phase. Well formed and outwardly uniform silicon crystallites of 150–200 μm dimensions were shown by electron microscopy to result from particles ~300 Å in diameter.

Reshetnikov[104] studied the structure of thin films of Sb_2S_3 prepared by sublimation in a nitrogen atmosphere at pressures below 4 mmHg. He ascribes the highly disperse structure of the condensate to the formation of aerosol particles from vapour molecules which had lost their excess kinetic energy by collisions with nitrogen molecules.

Gen and coworkers[105] have examined the disperseness of aluminium aerosols as a function of formation conditions. A sample of aluminium was evaporated from a heated tungsten wire at the centre of a water-cooled glass bulb 8 cm in diameter. The bulb was filled with hydrogen, helium, or argon at 1–36 mmHg pressure. The deposits on the wall of the bulb were examined by electron microscopy: as the gas pressure was increased, the average size of the spherical particles increased gradually at first, but remained constant after reaching a critical value. The limiting particle diameter depends on the nature of the gas (~500 Å for He, ~700 Å for H_2, ~1500 Å for Ar). Depending on the disperseness, the colour of the films varied from black (for the finest particles, ~200 Å) to light grey (for condensates consisting of particles ~1500 Å in diameter).

Additional evidence has been published[106,107] in support of the view that the black deposits obtained by the evaporation of various metals (Au, Ag, Bi, Pb, Cd, Zn, Sb, Sn) in various gases (air, nitrogen, argon) at pressures < 0.5 mmHg consist of aerosol particles.

Rosinski and Snow[108] developed a model of the combustion of meteorites in the earth's atmosphere with formation of secondary aerosol particles by evaporating iron (using the exploding wire method) in argon, oxygen, and argon–oxygen atmospheres at pressures of $(1-4.1)\times10^{-3}$ mmHg. The grid supporting the collodion film for electron microscopy was located in a side arm, where it was accessible to atomic aggregates only by diffusion. Aerosol particles ≤ 300 Å in diameter were formed at a pressure of 4.1×10^{-3} mmHg. Particles of iron oxide were obtained in an oxygen atmosphere. These workers used Smolukhovskii's coagulation theory to derive a system of differential equations describing the change in concentration of the various aggregates, and computed the size distribution of secondary particles as a function of time after the instantaneous evaporation of a meteor in the earth's atmosphere.

Karioris and coworkers[109–111] also described an aerosol generator based on an exploding wire, and prepared aerosols of various metals. Particles ~ 1000 Å in diameter were obtained in a nitrogen atmosphere. An X-ray diffractometer was used to show that under these conditions nitrides are obtained from Al, Fe, In, Ta, Th, V, W, and Zr. The Au, Ag, and Mo condensates contain practically pure metal. It was shown that explosion of Ag, Au, and Pt wires in air, and of Cu and Al wires in argon, gives aerosols of the pure metal, whereas explosion of base metal wires in air gives aerosols of the oxides. In addition to the fine particles (0.1–0.01 μm), relatively coarse particles resulting from the splash of the molten metal were detected.

Kimoto and coworkers[112] made an electron microscopic and electron diffraction study of the condensates of many metals (Mg, Al, Cr, Mn, Co, Ni, Fe, Cu, Zn, Cd, Ag, Au, Sn, Pb, Bi) obtained in the presence of various pressures of argon on a collodion film. They observed separate particles, both faceted and spherical, of size increasing from hundreds to thousands of Ångstroms as the argon pressure was increased from 1 to 35 mmHg. The aerosol particles in these experiments are assumed to be formed by condensation of the vapour on impurities. This view is hard to accept. If the impurities can act as condensation nuclei in the vapour more readily than the metals themselves, the mechanism is far from self-evident, particularly since the concentration of impurities in most of the metals was low, and yet aerosol particles were obtained in all cases.

Gen and coworkers[113] obtained spherical aerosol particles of Ag–Cu alloy, in which the solubility limits of the macroscopic alloys were largely exceeded, by the simultaneous condensation of the metal vapours in a gaseous carrier (Ar, He). The conditions for the formation of highly disperse alloys, and methods of determining their composition, are also discussed in that paper.

The problem of the origin of the atomic aggregates (whether emitted by the evaporation surface or formed above the evaporation surface) must be solved in each individual case. In 1914, Swann[114] had suggested that polyatomic complexes can evaporate from a metal in order to account for the electrical conductivity of thin metallic films. The assumption is to some extent confirmed by mass-spectroscopic measurements. Petrov and Rusin[115] obtained additional information in their study of the condensation of aluminium vapour on glass at ~ 10^{-3} mmHg

pressure. They inserted a copper screen with a circular orifice in front of their glass plate, and obtained a narrow concentric ring surrounding the central spot which could only be explained by postulating a double reflection of the particles from the plate and from the screen. The particles travel in straight lines, conserving the momentum acquired during evaporation. Electron microscopy showed that both the central spot and the thin surrounding ring consisted of particles ~ 30 Å in diameter. Evidently, evaporation of aluminium gives rise to polyatomic complexes as well as to single atoms, and the complexes add on further atoms during their flight. (This conclusion is consistent with the mass spectrometric measurements[29].) On raising the residual gas pressure from ~ 10^{-3} to 5 × 10^{-2} mmHg a highly disperse black powder appears on the screen but the deposit on the glass plate remains specular. This observation confirms Levinstein's observation that a mirror-like condensate can be formed from aerosol particles at a particular pressure of residual gas[100].

Palatnik and coworkers[116-118] studied the effect of temperature of the inert gas (argon) on the size and shape of the condensate particles of various metals (Pb, Sb, Cd, Zn, Mg) and their alloys. They evaporated the metals from an alundum crucible within an aluminium cylinder which could be heated to < 350°. The Mg, Cd, and Zn could be evaporated by an electric arc. The argon pressure was varied from 3 to 90 mmHg. The deposits were studied by electron microscopy and X-ray diffraction, and the results were treated by assuming two separate condensation mechanisms (vapour → crystal and vapour → liquid → crystal). The predominance of either mechanism is critically dependent on the temperature of the gas, controlled by the cylinder walls. However, the authors ignore the fact that at these pressures of argon the aerosol particles are formed near the evaporation surface, where the temperature is determined mainly by the crucible rather than by the cylinder walls. Hence, the published electron micrographs[116-118] are more characteristic of the coagulation and sintering processes of the particles on the heated walls of the apparatus than of homogeneous condensation.

Condensates from alloys[116-118] showed the following behaviour. Alloys of the eutectic type (Pb–Sb, Bi–Zn) gave a mechanical mixture of aerosol particles of the components. Condensates from solid solution showing continuous solid solubility (Bi–Sb, Cd–Mg) consist of particles covering a wide range of concentrations. In the remaining cases (Pb–Bi, Cd–Sb, Mg–Sb, Mg–Bi) the diffraction patterns suggest simultaneous condensation of the components on nuclei of definite compounds. At high enough crucible temperatures and for short evaporation times the composition of the condensate is exactly the same as that of the initial alloy. For example, with Pb–Sb and Pb–Bi alloys evaporated in 20 s the composition of the deposit becomes the same as that of the initial alloy when the temperature is raised to 1200°, and remains unchanged at still higher temperatures. This result would appear to need confirmation, in view of the large difference between the vapour pressures of the components of these alloys, and of the fact that the rate of arrival of atoms of the more volatile component from the bulk of the melt is not constant.

Gen and coworkers[119] prepared highly disperse Fe–Co alloys containing between 0 and 100% of Co by the aerosol method. The particles prepared in argon and helium at atmospheric pressure (~ 500 and ~ 160 Å in diameter respectively) were spherical. As the Co content was increased, the alloys gradually passed through a one-phase region (α-Fe structure), a two-phase region (α-Fe and γ-Fe), and a one-phase region (γ-Fe), finally adopting the Co face-centred cubic structure. The lattice parameters of the aerosol alloys are different from those of bulk alloys with the same composition. The lattice parameters of Fe–Co aerosol alloys and of Fe and Co particles were shown to be smaller than those of the corresponding bulk phases, and to be a function of particle size.

A study of the coagulation of silver aerosol particles of ~ 30–50 Å primary diameter has been published[120]. The metal vapour issuing from an induction furnace was allowed to mix with a stream of cold air at 23–68 mmHg pressure. The aerosol was led along a tube and electrostatically precipitated at various distances from the furnace. The extent of coagulation was obtained from the number of particles found in the deposit. The absolute concentrations were measured by a radioactive silver isotope.

Palatnik and coworkers[121] studied the size and shape of Mg, Cu, and Al particles deposited in an argon atmosphere on rods variously oriented with respect to the evaporation source. As the authors themselves point out, the interpretation of the results is complicated by secondary growth and sintering processes on the rods.

Japanese physicists[122-125] studied the crystal structure and geometrical form of the aerosol particles of various metals prepared in argon. Again it was shown that as the pressure is increased the particle size increases from ~ 100 Å (at 1 mmHg pressure) to several tenths of a micron (at 30 mmHg). Particles less than 300 Å in diameter were spherical, whereas the larger particles had a normal outline. Addition of 0.1 mmHg of air to 6 mmHg of argon produced particles with a rounded (Au, Ag, Fe, Pb) or abnormal (Zn, Cd, Mg, Be) outline. No oxides were detected on the surface of the particles. Surprisingly, it was found that chromium particles prepared in pure argon had an unusual structure (lattice constant of unit cube a_0 = 4.588 ± 0.001 Å), whereas chromium evaporated in an argon–air mixture (6 mmHg + 0.1 mmHg respectively) gave well formed particles with a normal body-centred cubic lattice (a_0 = 2.88 Å).[124]

The formation of aerosol particles with a pentagonal or, less frequently, hexagonal profile by the evaporation of gold and silver in argon (12 mmHg) is extremely interesting[126]. Particles of this shape had previously been observed in gold and silver condensed in a high vacuum[127,128]. Electron diffraction showed that the decahedral particles (giving a pentagonal profile) consist of tetrahedra bounded by {111} planes in mutually twinned positions. The expected small angle of misfit in the combination of five tetrahedra was not observed. The hexagonal outline is produced by icosahedral particles composed of tetrahedra.

The most detailed study of gold "compound particles" is due to Komoda[129]: some of his electron micrographs (obtained in a high-resolution microscope) are shown in Fig. 1. It is interesting to note that the decahedral and icosahedral shapes are found in particles ~ 20 Å in diameter, and are retained up to 150–200 Å particle size. Coarser particles have a more complex structure, but they are free from dislocations.

Wada made a comparative study[130] of the formation of Mg, Zn, Cd, Al, Fe, Cu, and Ag aerosol particles in helium and argon at pressures between 1 and 600 mmHg. His results are in qualitative agreement with the conclusions of Gen and coworkers[105]: particles are formed in a condensation zone whose width increases as the gas pressure is decreased; the particle size increases with gas pressure; for equal pressures, the particles are smaller and the condensation zone is larger in helium than in argon.

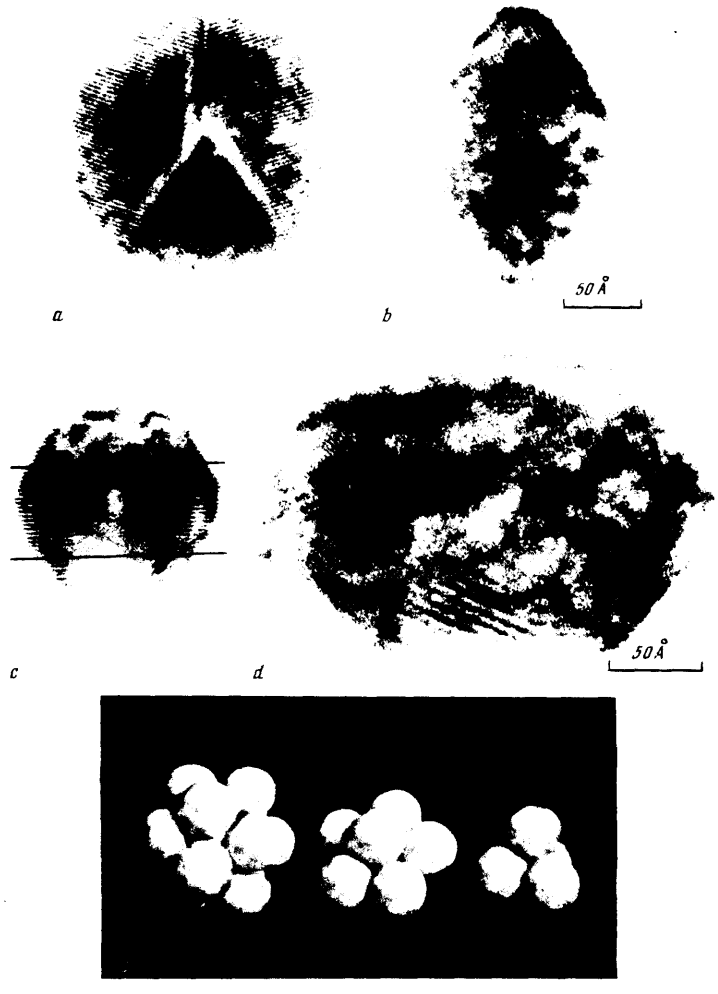


Figure 1. High-resolution electron micrographs of gold particles. The {111} planes are clearly visible. *a*) and *b*) show a small decahedral particle from above and laterally; *c*) is a small icosahedral particle with a hexagonal outline, the parallel straight lines are drawn to show the divergence of the lattice planes near the surface of the particle; *d*) is a larger particle of irregular shape, showing a complex internal structure; *e*) are models of the building of decahedral and icosahedral particles from the elementary tetrahedron

Particles of Fe–Co alloy of 100–700 Å diameter, prepared by evaporation in a low pressure of argon, are joined into long chains by magnetic forces[131].

Fukano and Kimoto[132] studied the structure of aerosol particles formed by evaporation of Ni–Pd, Fe–Ni, Au–Ni, and Ag–Pd alloys in argon. The particles had the same composition as the source alloy, and the composition dependence of their lattice parameter (face-centred cubic structure) was the same as for the bulk material within 2%. The aerosol particles of the Au–Ni alloy consisted of a solid solution which is normally stable only at high temperatures.

Highly disperse silver aerosols have recently been produced by evaporating the metal in argon and injecting the stream into cold air.[133]

The presence of an inert gas atmosphere enables new nuclei to be formed, and assists the coagulation of existing atomic complexes. On raising the gas pressure the average size of the metal aerosol particles initially increases to a limiting value, which is retained up to atmospheric pressure. This behaviour has an easy phenomenological explanation based on observations of fog formation. It is visually obvious that at high inert gas pressures the metal fog forms in a narrow region close to the vapour source: convective gas flow merely removes the particles from this "aggregation region", without appreciably affecting their size. When the gas pressure is lowered, the aggregation region widens, its inner boundary moves away from the evaporator, and its outer boundary moves closer to the

walls of the vessel. At the same time, the role of convective flow decreases and the role of diffusion increases. The mean particle size is affected by the gas pressure only when the outer boundary of the aggregation region reaches the wall of the apparatus. In this case the wall hinders the coagulation process which normally occurs in the bulk of the vapour–gas mixture.

No satisfactory explanation has yet been given of the limiting average particle size at high gas pressures or of the dependence of the limiting particle size on the nature of the gas [105,130].

The evaporated atoms come to thermal equilibrium with the gas very rapidly. According to Cravath's formula [134], the mean fractional loss of energy attending collisions between the atoms and the gas molecules is

$$f = \frac{8}{3}\frac{mM}{(m+M)^2}\left(1-\frac{T}{T_m}\right),$$

where m and M are the masses of the vapour atom and of the gas molecule respectively, T_m is the evaporation temperature of the atoms, and T is the gas temperature.

For example, in the evaporation of aluminium in argon $T_m \simeq 1800°K$, $T \simeq 300°K$, and therefore $f \simeq 0.53$, i.e. the energy of the atoms decreases by about a factor of two at each collision.

Rosin and Rabi [135] measured the mean free path of the evaporated atoms of alkali metals in various gases. From their results, summarised in Table 3, it is evident that the mean free path λ of the atoms is of the order of 1 mm at a gas pressure $P \simeq 10^{-2}$ mmHg. Hence, the atoms must come into thermal equilibrium with the ambient gas within a short distance from the evaporation source. Under these conditions, polyatomic complexes can be formed.

The effect of the complexes on the rate of evaporation of the metal has been studied [136]. The theoretical conclusion is that the diffusion layer of complexes which exists close to the evaporation surface in an inert gas atmosphere has no effect on the mass transport: hence, if the evaporation is limited by mass transport, the rate of evaporation is the same as for an atomic vapour.

Mizushima [107] tried to obtain a criterion for the formation of aerosol particles from the familiar expression for the number of atomic three-body collisions. Assuming that the higher complexes are formed by successive increments of single atoms, he obtained the approximate expression

$$\frac{Z_{n+1}}{Z_n} \approx \tau_n \frac{u}{\lambda},$$

where Z_{n+1} and Z_n are the numbers of collisions per second between atoms and complexes of $(n+1)$ and n atoms respectively; τ_n is the life time of the n-atom complex; u is the mean velocity and λ is the mean free path of the atoms.

Mizushima proposes the following inequality as the condition for the growth of particles:

$$\frac{Z_{n+1}}{Z_n} \geqslant 1, \quad \text{i.e.} \quad \tau_n \geqslant \frac{\lambda}{u}.$$

Taking $\lambda = 10^{-3}$–10^{-2} cm and $u = 10^4$–10^5 cm s^{-1} at $T \simeq 1000°K$, he obtains $\tau_n \simeq 10^{-7}$ s.

However, a growing particle must pass through the stage of association corresponding to a low value of n, for which $Z_{n+1}/Z_n \ll 1$. Hence, Mizushima's criterion is not realistic.

The most fruitful collisions are those between two atoms of the metal and a polymeric complex of the gas. Under these conditions the energy of combination of the atoms to give a dimer is transferred to internal degrees of freedom of the complex, which may undergo dissociation. Thus, the heat of condensation of the atoms can be dissipated without heating the gas. Dimers, trimers, etc. can then unite to give larger particles.

Table 3. Values of $P\cdot\lambda$ in units of 10^{-4} (P is the gas pressure in mmHg, λ is the mean free path of the metal atoms in cm)

Gas	Li, 860 °K	Na 700 °K	K 620 °K	Rb 590 °K	Cs 560 °K
H_2	16.2	8.30	5.44	4.24	3.20
D_2	18.6	8.74	5.85	4.65	3.65
He	22.6	12.52	8.32	6.50	4.89
Ne	22.5	10.94	7.77	6.65	5.41
Ar	11.4	5.90	4.22	3.75	3.34

Other conditions being equal, the size of the particles is practically independent of the rate of evaporation. This result suggests a relationship between the number of condensation centres and the rate of evaporation. The primary condensate particles (subcrystallites) can be bounded by close-packed crystal planes. For example, the smallest subcrystallite of a face-centred cubic metal is a tetrahedron consisting of four atoms and bounded by a family of {111} planes. Since the formation of a new layer on close-packed faces requires a high supersaturation [54,137], most of the atoms will be simply reflected from the close-packed faces of the subcrystallite. Hence, the formation of new subcrystallites (which can aggregate into aerosol particles by collision) becomes more favourable than the growth of existing subcrystallites at some stage in the dynamic condensation process. This seems to be the most likely explanation of the relative insensitivity of the aerosol particle size to the rate of evaporation. Strictly regular packing of the subcrystallites in the particle cannot be expected: some randomness in the mutual orientation of the subcrystallites is unavoidable. The molecular force field will have almost spherical symmetry, and the subsequent growth of the particle (by adding on more subcrystallites) will bear a similarity to the growth of a snow-ball. In practice, nearly all the metal aerosol particles examined in the writer's laboratory were found to be approximately spherical. Fig. 2 shows a crystalline particle of cobalt $\sim 10^{-5}$ cm in diameter photographed at high magnification ($\sim \times 300\,000$) in an electron microscope with ~ 10 Å resolution. The total absence of facets is obvious. Examples of the ordered grouping of tetrahedral subcrystallites in small gold particles (20–50 Å), and of the disordered grouping in larger particles ($\geqslant 150$ Å), are shown in Fig. 1.

The important role of subcrystallite coagulation in the formation of spherical aerosol primary particles, and in determining the size distribution in a given range of vapour concentrations, is stressed in a recent review by Fuks and Sutugin [138], and also by other workers [120,133,139].

In what follows we shall use the term subcrystallite to denote structural groupings of atoms ranging in size from the smallest possible unit cell to 20–30 Å, and bounded mainly by close-packed planes. X-Ray studies of phase transformations in aerosol particles have confirmed that their structure is subcrystalline [140,141]. Observations of ferromagnetic resonance in nickel, cobalt, and iron particles [142,143], and of plasma resonance in silver and copper

particles[144], and also of the temperature dependence of X-ray scattering[145,146], are consistent with this point of view.

Only a fraction of the subcrystallites, determined by the inert gas pressure, is able to coagulate in the gas volume: the remainder reaches the walls of the vessel. When these migrate over the surface of a solid, and experience the orienting effect of the substrate, they can give rise to well formed crystallites. The speed and direction of migration of the subcrystallites depends on their size, on the temperature and topography of the surface, on the presence of adsorbed impurities and external fields, etc.



Figure 2. Aerosol cobalt particle. Facets are completely absent though the particle has a crystalline structure

Most of the platelet-like crystallites so far obtained (Mg, Cd[112], and Zn[100,112]) by evaporating a metal in an inert gas atmosphere originated almost certainly at the surface. The grids and films used by Kimoto and coworkers[112,122] may have been heated quite significantly by radiation from the evaporation source, and this will have assisted the surface migration of subcrystallites. It has been shown[144] that silver condenses on a glass substrate 7 cm from the evaporator under 0.15 mmHg argon pressure in the form of islets consisting of a large number of sintered particles ~ 20 Å in diameter, whereas on removing the substrate to a distance of 15 cm coarser, isolated aerosol particles are obtained. The former deposits have a specular reflection, the latter are black. The black deposits exhibit plasma resonance under normal light incidence; the specular deposits do not, indicating a difference in electronic conductivity between the isolated and the sintered particles.

By suitable choice of evaporation conditions (gas pressure, position, and temperature of substrate), metal deposits of mixed origin can be obtained. An example is shown in Fig. 3, where a long chain of spherical particles held together by magnetic forces appears side by side with faceted particles of iron[112]. These chains are similar in size to the ferromagnetic particles of iron, nickel, and cobalt which are typical of condensates from the gas phase[119]. In a large enough vessel ($\geq$ 25 cm in diameter), and with an argon pressure of ~ 0.1 mmHg, spherical particles of most metals are usually obtained on the cold walls as condensates formed in the gas. These particles are sometimes amorphous (for example, aluminium[147] and bismuth[140]). However, larger particles ($\geq 10^{-5}$ cm) of low-melting metals can develop facets if their residence time in the hot gas is long enough. Kimoto and coworkers point out[112] that the lack of facets in particles less than a few hundred Ångstroms in diameter should not be dismissed as insufficient resolution in the electron microscope: it is an important aspect of the growth mechanism of the crystal. Under comparable preparative conditions, different metals give deposits with a narrow particle size distribution and approximately the same disperseness, but the higher-melting metals produce significantly smaller particles. Fig. 4 shows the integral and the differential size distribution of Bi, Pb, Sb, and Ag particles prepared by evaporating the metals from a hot tungsten wire in argon at 0.1 mmHg pressure in a glass bell-jar 25 cm in diameter.

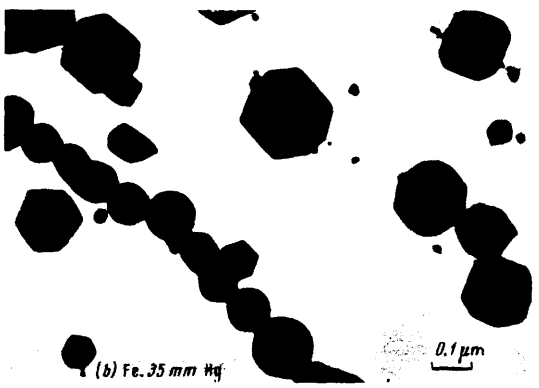


Figure 3. Iron condensate on a collodion film, prepared in a magnetic field of ~ 1000 Oe under an argon pressure of 35 mmHg.[112] The faceted particles have grown on the surface of the substrate, whilst the chain of spherical particles must have been deposited from the gas phase

The actual colour of the macroscopic metal deposit gradually darkens as the particle size decreases. This trend is particularly noticeable with non-ferrous metals such as gold, silver, and copper. Complete oxidation of the particles produces a colour change. Thus, black powders of iron and lead develop the characteristic colour of the oxides (dark red and white, respectively) after being heated in air. The importance of the correct gas pressure during the preparation of the blackened sensitive areas of radiation detectors has been pointed out[148]: it is shown that a layer of black having reproducible optical characteristics can be prepared by evaporating Bi or Sb at 0.1–0.4 mmHg pressure.

The physicochemical properties of aerosol particles have been discussed in a number of papers, which we shall briefly mention below.

Harris and coworkers[149] discuss the sintering of gold aerosol particles. Gen and coworkers[147] studied the crystallisation of amorphous aluminium particles prepared under controlled conditions. Exposure of a photographic emulsion by the oxidation of aluminium particles (the Colson–Russell effect) has been observed by Petrov and coworkers[150–152]. The oxidation process, and the structural changes in the oxide skin surrounding aluminium particles, have been examined by Petrov and Bibilashvili[152]. Petrov made a detailed investigation of the thermal expansion, phase transformations, melt structure, and temperature dependence of X-ray scattering in aerosol particles of aluminium[146,151,153], lead[140,146,154], bismuth[140,146], antimony[140,146], nickel[145], cobalt[155], tin[141,146], silver[156], iron[157], and cadmium[158].

The optical properties of Al, Ag, Cu, and Se particles were investigated by Petrov[144]. Plasma resonance in Al particles, excited by fast electrons, has been discussed by Fujimoto and coworkers[159,160].

Gen and Petinov[161] studied electron paramagnetic resonance in lithium particles. Nuclear gamma-resonance was observed in particles of tin[162] and of an Fe–Ni alloy[163].

Petrov and coworkers measured the ferromagnetic resonance of nickel, cobalt, and iron particles[142], and also the magnetic and dielectric permeability of nickel suspensions in paraffin oil at a frequency of 9320 MHz.[143]

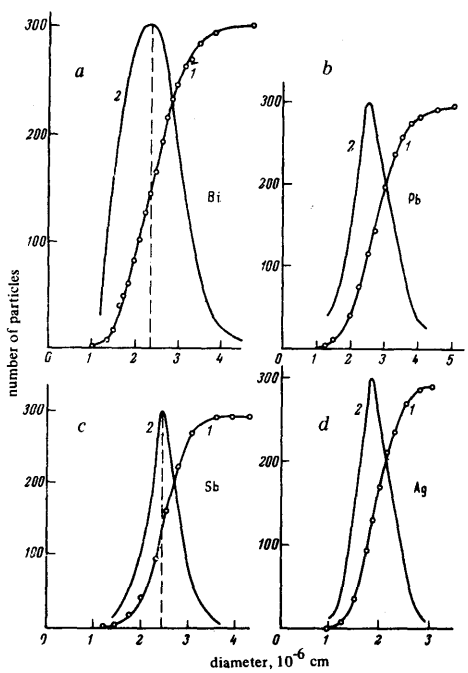


Figure 4. Size distribution of bismuth, lead, antimony, and silver aerosol particles prepared in a glass bulb 25 cm in diameter under ~ 0.1 mmHg argon pressure: *1*) integral distribution; *2*) differential distribution

The magnetic properties of Fe, Co, and Ni aerosol particles and of some of their alloys have been studied by several workers[131,164,165].

The hypothesis of a highly disperse structure of matter in the liquid and the solid state has been repeatedly proposed[166–183]. Experiments with aerosol particles are consistent with this hypothesis. Isolated subcrystallites, regularly assembled into a massive crystal, are assumed to be surrounded by a structureless (amorphous) layer of atoms which acts as an "inner lubricant". The thickness of the amorphous layers increases with temperature as a result of the "evaporation" of atoms from the surface of the subcrystallites, and this produces an increase in the rotational amplitude of the subcrystallites. At the melting point the subcrystallites enter a state of free random rotation: this is consistent with the appearance of an amorphous halo in the diffraction pattern of the liquid and with the vestigial structure of the original crystal found in the melt. The frequently reported "pre-fusion" of metals and associated specific heat anomalies[182–186], the increase in self-diffusion[187–189], and other phenomena[182] all point to a "loosening" of the bonds between subcrystallites[174] and to an increase in the thickness of the intervening amorphous layer. Lead particles ~ 200 Å in diameter close to the melting point have been shown to consist of approximately 115 face-centred cubic subcrystallites giving approximately 7 unit cells on each edge. On raising the temperature of the melt by 300° the size of the subcrystallites decrease only by a factor of 1.5.[154] It appears that the subcrystallites disappear completely only on approaching the critical temperature of the liquid–vapour transformation, when the melt adopts the uniform structure of a dense gas with the equilibrium distribution of polyatomic complexes. On cooling the melt, subcrystallites reform and gradually grow in size. Finally, the subcrystallites begin to touch one another, and an ordered array becomes energetically more favourable: in other words, the melt solidifies. The phase transformation is an avalanche-like cooperative process. The most convincing proof of the subcrystallite structure of aerosol particles is obtained by direct electron microscopy[126,129] (Fig. 1), and also by observing the anomalies in the coefficient of expansion of Al, Pb, Ag, and Cd particles close to the melting point.[158]

This secondary, disperse structure of matter in all three states of aggregation is due to kinetic processes on an atomic scale which are almost impossible to avoid in practice. Even carefully grown crystals exhibit a secondary structure in spite of the fact that an ideal single crystal of unlimited size is thermodynamically favoured. Thus, Delisle and Davis[190] observed a fine structure of particles ~ 1000 Å in diameter in copper crystals grown from the melt within the familiar mosaic blocks.

In some cases, crystals grown from the vapour in an inert gas atmosphere develop as a regular array of aerosol particles, especially when the latter show a narrow size distribution. Layer growth and dendritic growth of crystals can be explained by this mechanism.

It was pointed out long ago[191,192] that the thickness of layers at crystal faces is comparable to the size of the elementary cell (i.e. is larger than atomic dimensions, in contrast to the requirements of the dislocation theory). Growth steps up to ~ 1000 Å high[192] present insurmountable difficulties to the dislocation theory. Frank[193] was forced to postulate an empty channel at the centre of a dislocation with such a large Burgers vector: the function of this channel is to relieve the concentration of elastic energy which would otherwise exceed the mechanical strength of the material. No experimental evidence of the existence of this channel has yet been produced.

Spiral steps 0.1–1 μm high have been observed on the surface of various crystals (copper[194,195], lead[196], cadmium[197], germanium[198], silicon[199]). These are clearly associated with atomic groupings rather than with single atoms.

Sears[200] ascribes the formation of screw dislocations with a large Burgers vector to the collision of a growing ideal crystal platelet with an obstacle in the form of a colloidal particle. Lang[201] showed that random growth "faults" in the early stages of the formation of a step must result in a continuous spiral step of indeterminate height rather than in a circular step.

Evidently, subcrystallites or small aerosol particles of approximately uniform size can be packed as parallel layers on a growing solid surface, whereas the larger

particles or surface defects can provide the obstacles postulated by Sears and Lang to explain the large growth spirals found in crystals.

Straumanis[202] made the first experiments on the growth of Mg, Zn, and Cd crystals from the vapour in an inert gas (hydrogen) atmosphere. The metals were evaporated within a glass tube along which a temperature gradient was imposed. Well faceted crystallites up to a fraction of a millimetre in size were obtained under suitable conditions of hydrogen pressure and evaporation temperature. For hydrogen pressures above some well defined limit (~ 4 mmHg for Zn), platelet-like Zn and Cd crystals were grown. Mg gave loosely adherent thick layers when the pressure was raised to 0.5 atm. Thin layered Cd crystals were formed at hydrogen pressures of the order of 1 atm. The growth of metal crystals from the vapour in an inert gas atmosphere is discussed in a number of papers[203-208]. Keepin[203] studied the growth of Cd and Zn crystals from the vapour as a function of the evaporator temperature (molybdenum crucible), substrate temperature (Ag for Cd, Cu or Ni for Zn), and pressure of purified nitrogen (between 10^{-5} and 760 mmHg). Large but imperfect crystallites were obtained at nitrogen pressures > 0.5 mmHg. Dendritic crystals were predominant in the pressure range 10^{-2}–10^{-1} mmHg and substrate temperatures 250–350° (for Cd) and 200–350° (for Zn). Under the conditions listed in Table 4, large and well developed hexagonal crystals were grown. Under still lower pressures, and substrate temperatures close to room temperature, a few dendritic crystals were obtained but the deposits were predominantly amorphous (particle size ~ 100 Å, estimated from the X-ray line widths).

Table 4. Optimum conditions for the growth of Cd and Zn single crystals from the vapour in a nitrogen atmosphere[203]

Metal	Evaporator temp., °C	Partial vapour pressure, mmHg	Substrate temp., °C	Nitrogen pressure, mmHg
Cd	310–321	$\sim 10^{-1}$	305±3°	10^{-2}–$5\cdot10^{-2}$
Zn	409–419	$\sim 2\cdot10^{-1}$	410±3	10^{-2}–$3\cdot10^{-2}$

Keepin suggests that the removal of the heat of crystallisation is affected by the pressure dependence of the convective flow of inert gas: as a result, the shape and size of the crystals growing on the substrate by the addition of single atoms show a considerable variation. Coleman and Sears[204] studied the influence of inert gases on the growth of Zn, Cd, and Ag from the vapour. Filamentary growth ("whiskers") was observed in the presence of hydrogen or helium at 10–600 mmHg pressure. The whiskers were formed both on the growing Zn crystals and on the glass or quartz substrates. Some individual whiskers were up to ~ 17 mm long and 1–3 μm in diameter. The diameter of the whiskers decreased with increase of gas pressure, reaching a few tenths of a micron at 600 mmHg hydrogen pressure. Coleman and Cabrera[205] observed Zn and Cd whiskers 1–2 mm long and 1–10 μm in diameter, grown from the vapour in an inert gas at atmospheric pressure.

Price[206] grew Cd crystals from the vapour on a quartz fibre in an argon atmosphere. The temperature T and degree of supersaturation η were calculated at all points along the fibre, and a critical value ($\eta \simeq 0.4$) was noted below which no crystals grew. For $\eta \leqslant 2$, thin platelets and whiskers grew together on the filament irrespective of T and η; for $2 \leqslant \eta \leqslant 10^2$ thick hexagonal platelets were obtained; branching dendrites appeared and grew to a large size for $\eta \geqslant 10^2$ and $T \leqslant 250°$. Cd and Zn crystals have been grown[207,208] from the vapour in 10–600 mmHg of argon on the wall of a glass tube. Both platelet-like microcrystals and whiskers (up to 10 mm long and 1–5 μm in diameter) were obtained.

In all the work mentioned above[202-208] the rate of growth is assumed to be determined by the diffusion of atoms in the inert gas, and controlled by the degree of supersaturation of the vapour. The formation of aerosol particles, and their combination to give microcrystals, are ignored in spite of the fact that most of the evaporated material must have passed through the stage of aerosol condensates at the inert gas pressures used in this work. Aerosol particles are formed in all systems where crystallisation from the vapour phase is assisted by chemical reactions such as transport reactions and vapour-phase reactions[209,210]. This factor must be considered when analysing the mechanism of the process.

4. MECHANISM OF CONDENSATION OF A METALLIC VAPOUR ON A SOLID SURFACE

The primary stage in the formation of a metallic condensate on a solid surface is a very complex problem with many controversial aspects. Most workers (see previous reviews[57,211-213] and some more recent papers[214-221]) correlate the structure of condensed metal films exclusively with atomic processes at the substrate surface. The role of polyatomic vapour complexes is completely ignored.

Two different explanations have been put forward for the formation of small particles in the early stages of film deposition: they can be termed the "gradual" and the "spontaneous" nucleation mechanism respectively[222]. During "gradual" nucleation of particles the atoms of the deposit move over the substrate until they have lost their thermal energy and become attached at random or at preferred surface sites. "Spontaneous" nucleation of particles occurs in the amorphous or quasi-gaseous state at some critical concentration of deposited material.

According to Semenov[223], adsorbed atoms can be treated as a "two-dimensional" vapour which condenses on reaching some critical supersaturation.

Some of the earliest workers[224-230] had noted the existence of a critical surface temperature T_{cr} above which the metal vapour will not condense. T_{cr} was shown to be a function of the density of the molecular beam. Frenkel[231] put forward an explanation, involving the adsorption of all the impinging atoms, by further developing Langmuir's ideas[232]. If two atoms combine into a dimer during their life time in the adsorbed state, the latter can act as a centre for further condensation of atoms because the probability of secondary evaporation is lower for polyatomic surface species. However, at low beam densities the dimer can dissociate before the attachment of a third atom: obviously, in this case no film is formed. Because of the clear physical picture offered by Frenkel's theory, various modified theories were subsequently based on it.[57,212] On the other hand, the experimental fact that T_{cr} varies with time[233,234] lies outside the scope of this theory. Furthermore, theoretical calculations[235-237] suggest that metal atoms should always be adsorbed on a solid surface at all

experimentally accessible evaporation temperatures. Yet, supersaturations of $\sim 10^{15}$ or more are often needed in molecular beam experiments to induce significant condensation. Sears and Cahn[242] tried to resolve this drastic shortcoming of the theory of surface film nucleation by postulating a slow transfer of energy for atoms in the adsorption layer. According to these workers, the temperature of the layer must be intermediate between those of the substrate and of the evaporator. By modifying Frenkel's theory they concluded that for a constant beam intensity and a fixed substrate temperature there must be a critical evaporation temperature above which no nuclei are formed on the substrate.

Hudson[243-245] studied the formation of Zn, Cd, and Se crystal nuclei on glass and noted large discrepancies between the observed rates of condensation and those predicted by the classical theory. His explanation is analogous to that of Sears and Cahn[242], since he assumes a temperature of the adsorbed layer of condensate intermediate between the substrate temperature and the evaporator temperature.

However, Shade's experiments[241] with a cadmium molecular beam condensing on polyethylene films have shown convincingly that the results are independent of evaporator temperature, and hence that the theory of Sears and Cahn is incapable of explaining the enormous supersaturations ($\sim 10^{17}$–10^{20}) needed to initiate condensation.

Evseev and Ozhegov[246] have recently shown that for a fixed density of the molecular beam T_{cr} increases with beam temperature, whereas for a fixed substrate temperature the critical beam density decreases with increase of beam temperature. These results are not inconsistent with Shade's conclusions, since (as the authors themselves point out) the antimony vapour in their experiments probably consisted of 4-atomic complexes which could have dissociated on collision with the substrate. Gretz[217,220] tried to explain Hudson's experiments[243] on the condensation of Zn vapour on glass by refining the classical fluctuation theory of heterogeneous nucleation[76,247]. He introduced into the expression for the free energy of formation of a cap-shaped nucleus a term for the linear tension along the interface with the substrate. However, the theory of Gretz, like other variants of the classical theory based on the Gibbs–Kelvin equation, is not applicable to very small nuclei.

The very low observed rates of formation of Zn nuclei on glass and on mica[243] can be ascribed to a low thermal accommodation coefficient $\alpha_T = (T_0 - T_a)/(T_0 - T_s)$, where T_0, T_a, and T_s are the temperatures of the beam, the adsorbed atoms, and the substrate respectively.

If full thermal accommodation of the atoms is not achieved (i.e. $\alpha_T < 1$), the adsorbed layer will be at a higher temperature than the substrate, and the real supersaturation (η_a) will be correspondingly lower. Gretz attempted[219] to evaluate α_T from experimental data for η_a without resorting to the detailed equations of the theory of nucleation. He started from an empirically established linear relationship[57] between $\ln \eta_c$ and $(1/T_s)$, where η_c is the apparent critical supersaturation defined as the ratio of the effective vapour pressure in the beam to the vapour pressure corresponding to T_s. Assuming α_T independent of temperature, he postulated that $\ln \eta_a$ must also be linear in $(1/T_s)$, i.e. that the condition $\partial^2 \ln \eta_a / \partial (1/T_s)^2 = 0$ must obtain. In spite of these arbitrary assumptions, he obtained the reasonable values $\alpha_T = 0.993$ and $\alpha_T = 0.998$ for the condensation of Zn on glass[243] and on mica[248] respectively.

Hirth and coworkers[249] explain the discrepancy between Hudson's results[243] and the theory by pointing out that at low supersaturations stable nuclei are more likely to be formed by collisions between nuclei of subcritical size than by the addition of single atoms to critical nuclei.

Moore[250] has reviewed recent work on the condensation of metals on solid substrates using emission and electron microscopy. He also concluded that small atomic groupings have a high mobility which allows them to coalesce like liquid drops. Gretz observed[218] the sudden formation and the rapid growth of a silver nucleus in the emission microscope. Curzon and Kimoto[251] studied the condensation of lead vapour on molybdenite in an electron microscope, and observed an ordered deposition of small drops on surface microdefects of the substrate, which was heated to 350°. Ciné-photography was used to demonstrate the high mobility and the coalescence of the drops. The Brownian motion of 20–30 Å gold crystallites prepared by condensing the vapour on a KCl slip in a vacuum of 8×10^{-9} mmHg has recently been demonstrated experimentally[252].

Walton tried to resolve the uncertainties which arise when the concept of surface energy is applied to very small particles. He derived[253,254] a formula for the frequency of formation of nuclei in terms of the density of adsorbed atoms, the heat of adsorption of an atom, the dissociation energy of the critical nucleus, and the activation energy for surface diffusion. According to his model, configurations of two, three, etc. atoms on the substrate remain in stable equilibrium with the vapour phase until the critical supersaturation characteristic of each configuration is reached, when the shape of the nucleus suddenly changes. This theory was applied to the growth of oriented layers[255,256]. The possible orientation and the shape of the atomic groupings formed on a crystalline substrate by vapour condensation have been discussed theoretically by Halpern[216].

The growth of single-crystal films is a very complicated problem. The quality of the film depends on many factors, often inadequately controlled (e.g. the background pressure of residual gases). Background gases can affect the kinetics of the process both in the gas phase and at the surface of the substrate. For example, changes in structure and texture formation are observed on changing from a low vacuum ($\sim 10^{-2}$ mmHg) to an ultra-high vacuum ($\sim 10^{-9}$ mmHg) in the condensation of Au, Ag, Ni, and Al films[257]. There have also been reports of residual gas effects on the properties of condensed films of tin[258,259] and indium[260].

Palatnik and Komnik studied the structure of condensates (Bi, Sb, Pb, Sn, and other metals) on a glass plate which was heated non-uniformly[213,261-263]. They noted a sharp discontinuity in the optical transmission of the deposits at a substrate temperature (T_n) approximately 2/3 of the melting point of the metal, which they ascribed to a difference in the size and number of particles on either side of this transparency boundary. This difference in the structure of the condensate is explained by different condensation mechanisms, assuming that the supersaturated "two-dimensional" metal vapour condenses by a vapour → liquid → crystal mechanism on the hot side of the substrate and by a vapour → crystal mechanism on the cold side.

Fisher and Anderson[264], in a recent study of the condensation of lead, showed that T_n can change from 189 ± 2° to ~ 245° whilst the residual gas pressure remains below 10^{-5} mmHg. They also showed that the difference in structure of the deposit on either side of the transparency boundary lies mainly in the development of facets and not (as had been assumed by Palatnik and Komnik[261-263]) in the

size and number of the particles. At substrate temperatures above T_n the particles of the deposit are almost spherical, with rudimentary facets, whereas at substrate temperatures below T_n the particles are elongated with well developed facets. Fisher and Anderson were critical of Palatnik and Komnik's double condensation mechanism, and they proposed their own explanation of the difference in structure shown by lead condensates. Quoting some calculations by Burton and coworkers[137], they assume that different facets of the lead crystallites melt at slightly different temperatures: in this way, the crystal habit of the particles becomes a function of the substrate temperature. Fisher and Anderson's arguments also explain the experimental fact that T_n is independent of film thickness[261-264].

Many of the problems raised by the initial stage of formation of metallic condensates become clearer when allowance is made for the possible adsorption of polyatomic aggregates from the vapour. These have a longer life time in the adsorbed state than single atoms, and hence they can act as primary condensation centres. It can be assumed that at high substrate temperatures only the larger complexes are retained on the surface, whereas single atoms and small associations are either reflected or rapidly re-emitted from the surface. On this model, it is not difficult to explain the existence of a critical temperature for the condensation of a vapour on a solid surface, its dependence on time and on the density of the molecular beam, and also the structural differences observed when the substrate temperature is non-uniform.

Many experimental observations provide direct evidence for the deposition of quite large particles (although rapid growth of the primary adsorbed polyatomic complexes cannot be entirely dismissed).

Thus, when the condensation of Cd and Zn molecular beams on a Formvar substrate is observed directly in the electron microscope[265], primary particles up to ~ 200 Å in size appear quite suddenly. Newman and Pashley[266] made an electron diffraction study of the condensation of copper vapour on silver, and detected the sudden appearance and subsequent rapid growth of oriented primary crystallites ~ 60 Å wide and ~ 12 Å thick. Particles ~ 100 Å in size, mostly concentrated along step edges, are observed when defects in freshly cleaved NaCl and KCl surfaces are decorated by vacuum sublimation of Au, Pd, Pt, and Ge on the heated substrate surface. In spite of the large difference in the numbers of particles found on the smooth areas and on the step edges of the surface, the particle size is approximately constant. Furthermore, gold particles deposited on glass and on small NaCl crystallites previously sublimed on the same glass surface are of practically uniform size, despite the fact that the concentration of particles is approximately 10 times higher in the former case[268]. These results are not easy to explain in terms of the growth of particles by surface migration of adsorbed atoms, since that mechanism predicts an inverse relationship between the size of the particles and their concentration (assuming a uniform density of the molecular beam).

The finely grained films obtained at low substrate temperatures are particularly interesting. During the 1930's, Kramer[271-273] prepared thin (~ 10^{-4} cm) amorphous films of a large group of metals (Fe, Ni, Pt, Zn, Sn, Cd, Sb, Ir, Al, Pb, Hg, Mo) by condensing their vapour on a glass surface cooled in liquid air using thermal evaporation or cathodic sputtering in a low pressure of hydrogen. When the deposits were heated above some well defined critical temperature their electrical properties showed a sudden, irreversible change, approaching the properties of the bulk metal. Kramer suggested that the metal atoms lose their kinetic energy by collisions with gas molecules, and are therefore unable to combine with the crystal lattice when first adsorbed on the surface. However, polyatomic complexes and subcrystallites must have been present in his experiments. At low substrate temperatures, these are not mobile enough to combine into ordered single-crystal blocks.

Gen and coworkers[274] studied the electron diffraction patterns of Fe, Ni, Cd, and Hg deposits (and also the electrical conductivity of Cd deposits[88]) prepared in a high vacuum on a glass surface at liquid-nitrogen temperature, and found a crystalline structure with a crystallite size of ~ 10^{-7} cm. These layers underwent recrystallisation on being heated, as shown by the sharpening of the diffraction lines and by the irreversible decrease (by a factor of 2–2.5) in electrical resistance[88].

Later work confirmed the conclusion of Gen and coworkers[274] that low-temperature condensates are apparently amorphous only because of the small size of the primary crystallites of which the film is composed.

More recent electron-diffraction studies[275] of Bi, Ga, Be, Fe, Cr, and the Pb–(12% Bi) alloy, condensed at 4.2°K, has revealed a similarity in radial distribution function between atoms in the films and atoms in the corresponding bulk melts. The size of the primary subcrystallites is estimated to be only a few Ångstroms. On raising the temperature to 77°K the films are converted from an amorphous into a crystalline structure, with a crystallite size of the order of tens of Ångstroms. The same author[276] demonstrated the amorphous structure (subcrystallite size of the order of Ångstroms) of Ti, Mn, Co, Pd, Y, and Fe–Ni, Ag–Cu alloy films condensed in a high vacuum on a cooled substrate (77°K).

Grigson and Barton[277] have reviewed existing electron diffraction calculations for very small crystallites, and have developed a method of evaluating the Debye interference function for an assembly of identical, randomly oriented face-centred cubic subcrystallites containing from 2 to 9 atoms on an edge. By comparing the calculated diffraction patterns of liquid lead and of thin films of Pb, Ag, and Fe, it was shown[278] that the aggregates form an amorphous structure similar to that of a monoatomic liquid during the early stages of film growth (up to 10 Å).

Measurements of the line width in electron diffraction patterns of Cu, Al, Ti, Pb, Sn, Zn, In, Tl, and Hg condensates on a collodion substrate at 20 and 4.2°K indicate a primary crystallite size of ~ 30–100 Å.[279,280] When the films are annealed at a higher temperature their grain size increases and their electrical resistance decreases irreversibly.

During evaporation from the metal, single atoms are emitted together with polyatomic complexes, which become overgrown with atoms in the region of high vapour density close to the evaporator.

The structure and properties of the films are also determined by the angle of incidence of the molecular beam[281]. This effect is most probably due to the fact that the atomic complexes present in the vapour retain some directional motion along the surface when the incidence of the beam is not normal, whereas the single atoms are quickly scattered by the microscopic roughness of the surface. Furthermore, the larger aggregates are more readily oriented in the plane of the surface and are less easily influenced by the microscopic profile. This is consistent with the fact that oriented films on amorphous substrates are obtained much more easily by evaporating the metal in an inert gas

atmosphere than in a vacuum[282]. Thus, fully oriented Ni films with a {110} plane parallel to the substrate are formed on glass in the presence of a 1 mmHg background pressure of argon. These films had a BET surface area and a catalytic activity greater than those of films prepared in a high vacuum by a factor of 2 and 3–5 respectively[283]. Evidently, the vacuum condensates had been formed on smaller aggregates than the deposits obtained in an argon atmosphere.

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Several interesting papers on the preparation and properties of metal aerosol particles have appeared while the manuscript was in press.

Wada[284] has developed a method of volatilisation in a mixed hydrogen–helium plasma, aimed at improving the efficiency of the aerosol method. He obtained 100 Å particles of an Fe–Co–Ni alloy at a gas pressure of 250 mmHg.

Chopra and coworkers[285] prepared very thin films of W, Ta, Mo, Re, Hf, and Zr by evaporating the metal in an argon plasma; there can be no doubt that these films consist of very small aerosol particles. Very interesting structural modifications of the particles are observed at substrate temperatures of 200–400°. Wada has shown[286] that evaporation of many metals in a xenon atmosphere gives particles 3–4 times larger than the particles obtained under the same pressure of argon.

The critical temperature of the transition to the superconducting state has been shown to be abnormally high in granular films consisting of aluminium aerosol particles[287].

Nishida[288] made a detailed study of the shape and structure of manganese particles obtained by evaporating the metal in argon or xenon at low pressures. He observed particles of the high-temperature β-Mn modification as well as α-Mn.

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