MICROMETALLIC PARTICLES

D. CHAKRAVORTY
Advanced Centre for Materials Science, Indian Institute of Technology,
Kanpur 208 016, India.

INTRODUCTION

STUDY of ultrafine metal particles having diameters in the range 10 –200 Å dispersed in various media have attracted considerable attention in recent years because of their technological importance[1-4]. These materials also provide theoretically interesting systems to understand the physics of micro metal particles[5-7].

Cermets which are composite materials of metals and insulators with the metal phase having submicroscopic dimensions are used as electrical resistors because of the wide range of resistivity values that can be obtained in them and their low temperature coefficients of resistivity[2]. Small metal clusters dispersed on the surface of a suitable refractory oxide comprise an important group of catalysts which are extensively used in the chemical industry[4]. Electrolytically coloured anodic alumina coatings with a fine dispersion of cobalt metal are widely used in the building materials industry[8]. Cobalt alumina cermets are produced on an industrial scale for use in solar photothermal collectors because of their selective absorption of solar energy[9].

Dispersion of micro metallic granules in oxide glass media is exploited to make photo-sensitive glasses[10], glass-ceramics[10] photochromic glasses[11] polychromatic glasses[12] and solar control coatings[3]. In this paper we survey the various preparational methods developed so far for making ultrafine metallic particles, the important physical properties of these systems and the theoretical models used to explain the same.

METHODS FOR PRODUCING ULTRAFINE METAL PARTICLES

Evaporation technique:

In this method[13] a discontinuous film of the metal concerned is deposited on a suitable substrate (*e.g.* glass) under ultra high vacuum conditions ($< 10^{-9}$ torr) by evaporation from a resistively heated[14] or electron beam heated source[15]. The thickness of the films is in the range 10 200 Å. The metallic island size varies between 10 Å and 100 Å. The formation of these islands takes place by nucleation at many sites on the substrate followed by growth brought about by absorption of single atoms either impinging on the nucleus or migrating by surface diffusion on the substrate[16]. Island structure of metals such as copper[17], silver[18], and gold[19] have been investigated extensively. A variation of the above method is the discontinuous multilayer technique in which there are several layers deposited every second layer being a metal film in its island stage of growth[17,20]. The remaining layers consist of insulating continuous films.

Recently an inert-gas evaporation technique has been developed for making ultrafine metal particles in reasonable quantities by heating a large quantity of the metal in a temperature-stabilized oven[21]. The nucleation and growth in this method take place in a noble-gas atmosphere *e.g.*, argon. The metal vapour is cooled rapidly because of the collision of metal atoms with those of the gas. The critical size of the metal nuclei depends on the cooling of the metal atoms relative to the source temperature. As a result, critical diameters can be as low as a few angstroms if the metal particles are cooled by a few hundred degrees. These nuclei then grow in a layer above the surface of the hot metal. Ultrafine metal particles of Al, Mg, Zn, Sn, Cr, Fe, Co, Ni, Cu and Ga have been prepared by this technique and their structural features investigated by electron microscope[21]. Distribution of metallic particle sizes has been analysed which obeys the log-normal distribution function (LNDF) *i.e.* the fractional number of particles n per logarithmic diameter interval is given by,

$$\Delta n = \frac{1}{(2\pi)^{1/2} \ln\sigma} \exp\left[-\frac{1}{2} \times \left\{ \frac{\ln\left(\frac{x}{\bar{x}}\right)}{\ln\sigma} \right\}^2 \right] \Delta(\ln x) \qquad (1)$$

where x is the statistical median diameter and is the geometric deviation. This distribution is shown to arise due to the growth of particles by a liquid-like coalescence[21]. Such a growth model is found to account for the size distribution of particles produced by other methods such as colloids, discontinuous films and supported catalysts.

Closely related to inert-gas evaporation is the method of preparing fine metallic particles by exploding wires with current pulses in a noble-gas atmosphere. Examples are silver[22] and copper[23]. Particles have also been produced by homogeneous nucleation of metal vapour expanding with an inert carrier gas through a supersonic nozzle e.g., zinc[24].

Cermets are prepared by rf sputtering from composite metal insulator targets $\sim$ 15 cm. in diameter. Typical frequency[2] used is 12.56 MHz and the Ti sputtering is performed in purified A gas at a pressure 10^{-3} torr[26]. The substrates used are fused-quartz plates. Some of the cermet films prepared by this technique for detailed structural and electrical property investigation[2] are $Ni-SiO_2$, $Pt-SiO_2$ $Au-Al_2O_3$, $W-Al_2O_3$. Cermet films of $Ni-Al_2O_3$[26]. $Au-MgO$[35], $Cr-Cr_2O_3$[27] have been made and their optical properties delineated.

Chemical Methods

In most of the chemical methods of preparation, the ultrafine metal particles are dispersed in an inert medium—either a liquid or a solid—the latter being mostly a glassy substance.

In the Svedberg electrochemical method[28] a high frequency electrical arc is struck between metal clips under either a polar or a nonpolar liquid[21]. The metal gets vaporized, condenses in t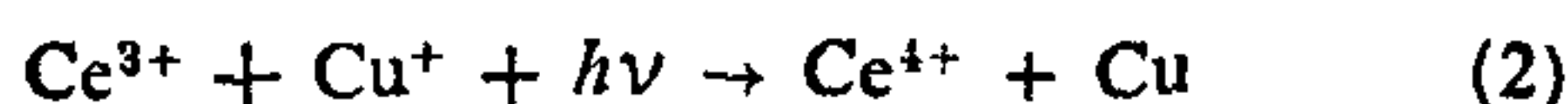he liquid and ultimately goes into suspension as tiny colloidal particles. Colloids are also prepared by chemical vapour deposition techniques. The structure of gold sols made by the reduction of $AuCl_3$ with formaldehyde[29,30] has been investigated[21]. A similar approach is adopted for preparing catalysts consisting of small metal clusters of platinum, osmium or iridium dispersed on the surface of alumina in a high surface area form[31].

Metals such as copper, silver, gold, platinum and bismuth can be obtained in colloidal form, in oxide glasses, if the latter are suitably reduced during melting[32,33]. The reducing agent used is either SnO or Sb_2O_3. In the case of bismuth no reducing agent is necessary.

Metallic micro-granules can also be precipitated in a surface layer (thickness of the order of a few micrometers) of an oxide glass by subjecting the latter to an ion-exchange and reduction treatment[36,37]. The requirement in this method is the availability of some alkali ions (e.g., Na^+Li^+) within the glass which can be exchanged with an easily reducible ion (e.g., Ag^+, Cu^+) present in a molten salt. The metal granules are formed in the glass by a nucleation and growth mechanism[37]. The nucleus density is found to be markedly dependent on the phase separation characteristics either incipient or induced by the ion-exchange step in the parent glass.
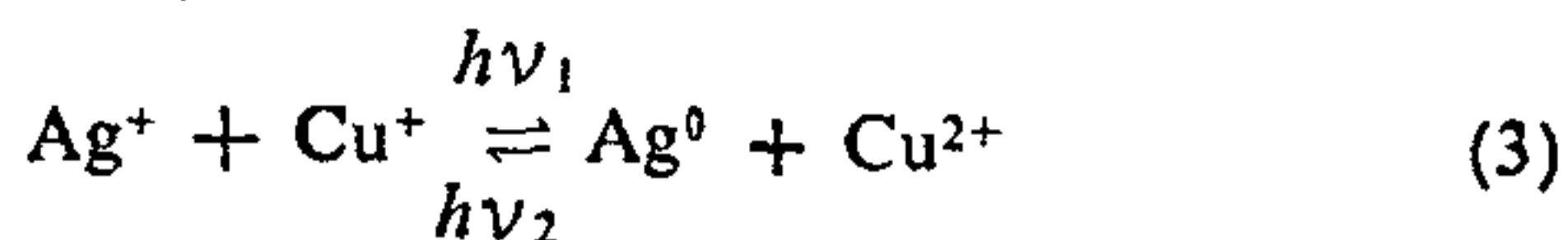
Photochemical methods:

In photosensitive glasses metallic colloids of copper, silver and gold respectively can be precipitated by subjecting the glasses to ultra-violet radiation followed by a suitable heat treatment[32]. The photosensitivity can be improved by the inclusion of a small amount of sensitizer e.g., CeO_2, Sb_2O_3. The reaction involved in the case of production of copper atoms, for instance, can be represented by,

$$Ce^{3+} + Cu^+ + h\nu \rightarrow Ce^{4+} + Cu \qquad (2)$$

In photochromic glasses which have a silicate network, a dispersion of crystals of silver chloride or a mixed halide (e.g., AgCl–AgBr) is developed by heat treatment[34] around 560° C. These crystals get decomposed by incident light into silver and halogen atoms. The darkening effect

caused is due to the presence of minute silver particles. A small amount of copper serves as a sensitizer for the above process. The reaction can be represented by

$$Ag^+ + Cu^+ \underset{h\nu_2}{\overset{h\nu_1}{\rightleftharpoons}} Ag^0 + Cu^{2+} \qquad (3)$$

A variant of the above method is the two stage u.v. exposures with heat-treatment schedules in between, as used for making polychromatic glasses[35]. The first exposure followed by the heat treatment leads to the precipitation of colourable pyramidal NaF (Na, Ag)X crystals (X: halogen atoms). The second exposure gives rise to the formation of silver specks at the tips of the pyramidal crystals.

PROPERTIES

(i) *Electrical*

Electrical properties of ultrafine metallic granules are usually analysed by considering these particles to be dispersed in an insulating medium thereby forming a composite[38]. The example taken for developing detailed theoretical model is that of granular metals or cermets[2]. These materials[39] show a metal—non-metal transition of the percolative type at a critical volume fraction value of 0.4–0.5 *i.e.*, there is a sharp rise in the electrical conductivity at this point. These values are higher than 0.15 which is expected for continuum percolation in three dimensions. Such a large percolation threshold has been ascribed to be due to the formation of oxide coatings on the metallic grains, though electron microscopic investigation does not confirm this. A more realistic explanation has been that the segregation of the metallic species into grains is incomplete so that some metal remains randomly dispersed in the oxide matrix[38].

For volume fraction below the percolation threshold, the structure of the composite consists of small, isolated metal particles dispersed in a dielectric continuum. Electrical conduction in this case takes place by the transport of elecrons and holes by tunelling from one isolated metal grain to the next. The resistivity[2] for low electric fields is given by,

$$\rho = \rho_0 \exp[2(C/kT)^{1/2}]. \qquad (4)$$

In this equation ρ_0 can be assumed to be a constant to a first order approximation and

$$C = Xs E_c^0, \qquad (5)$$

where $X = \left[\dfrac{2m\phi}{\hbar^2}\right]^{1/2}, \qquad (6)$

m being the electronic mass, ϕ the effective barrier height and $\hbar$ the planck's constant; s is the separation between the grains, E_c^0 is the energy required to generate a pair of fully dissociated positively and negatively changed grains and is given by,

$$E^0{}_c = 2_e{}^2/Kd, \qquad (7)$$

where $K' = \epsilon[1+(d/2s)], \qquad (8)$

ϵ is the dielectric constant of the insulating medium and d the grain size.

The above equations have been found to predict results which are in reasonable agreement with experimental data for cermet systems[2] Ni-SiO$_2$, Pt-SiO$_2$, Au-Al$_2$O$_3$ and oxide glass-bismuth[33,40,41] and oxide glass-silver particulate systems[42].

Electrical conduction in granular metals at high electric fields increases because of the additional mechanism of field-induced tunnelling. The expression[2] for electrical conductivity as a function of the electric field E is given by,

$$\sigma_H = \sigma_\infty \exp\left[-\frac{E_0}{E}\right] \int_{-E_{0L}}^{\infty} \frac{dz, z \exp(-z)}{1 - \exp\left(\frac{z}{z+E_0/E} \frac{EC_0}{E_0 kT}\right)} \qquad (9)$$

with $\sigma_\infty = \dfrac{e^2 Ir}{[(s_0+d_0)^2 (2Xs_0+1)^2 \hbar]} \qquad (10)$

$$C_0 = C\left(1+\frac{1}{2X s_0}\right) \qquad (11)$$

$$E_0 = \frac{C_0}{e(s_0+d_0)}, \qquad (12)$$

where s_0 and d_0 are the most probable values of s and d resepctively. Measurements of resistivity upto a field $\sim 10^6$ V/cm at temperatures ranging from 300 K to 1.4 K in the case of Ni–SiO$_2$ and Pt–SiO$_2$ cermets confirm the validity of the above theoretical model.

Glass-metal particulate systems with bismuth as the metallic species exhibit memory switching[43,44]. The threshold field is of the order of 10^4 V/cm and the resistance change between the "off" and "on" states is about two to three orders of magnitude. A particle stretching model has been used to explain this behaviour[45,46].

In the case of superconducting metals (*e.g.*, Al, Ga), there is a substantial enhancement in the transition temperature Tc when the volume fraction is larger than the percolation threshold[47]. This has been attributed to softening of the phonon modes[48,49].

(ii) *Magnetic*

Ni–SiO$_2$ cermets exhibit bulk ferromagnetism for metal volume fraction greater than 0.7[50,51]. An interesting property observed in this system for a volume fraction of 0.48 is a peak in the transverse magnetoresistance around 200 K for an applied magnetic field of 2700e[52]. Such a behaviour is due to a shift in the conduction path with temperature(at low temperatures it is superparamagnetic and at higher temperatures it is ferromagnetic).

The magnetic moment of small indium particles with a diameter $\sim$ 50 Å embedded in paraffin has been investigated at temperatures 1.5 K to 4.2 K in magnetic fields upto 50 KG[5]. The low saturation field observed for obtaining the saturation paramagnetic moment cannot be explained on the basis of electronic quantum size effects.

(iii) *Optical*

Extensive studies have been carried out on optical transmittance characteristics of cermet films like MgO–Au[25], Ni–Al$_2$O$_3$[26,53] and ultra-

fine nickel particles for developing selective black absorbers with high solar absorptivity and low infrared emissivity with a view to increasing the efficiency of flat-plate solar collectors. The measurements are usually made in the wavelength range 0.3–30 μm. The general feature of the results is high absorption over the solar spectrum and low absorption in the thermal infrared range. In the case of ultrafine gold particles[54], a large transmittance minimum is found around 0.6μm, whereas the samples show very little absorption at wavelengths above 1.5μm. Copper microparticles precipitated within an oxide glass by ion-exchange and reduction treatment show two absorption bands at 0.43μm and 0.57μm respectively[37]. Silver granules in oxide glasses precipitated by the same method show an absorption maximum at around 0.4μm[55].

Optical properties of an assemblage of micrometallic granules can be described in terms of an effective medium which comprises, a spatial average over the dielectric permeabilities for the metal islands (ϵ) and for their surrounding material (ϵ_m). This is valid because the particles under consideation have dimensions which are orders of magnitude smaller than the wavelengths of optical radiation. The simplest effective medium theory used to analyse experimental results in different systems[54] is that of Maxwell-Garnett[8,56,57], according to which the effective dielectric permeability $\bar{\epsilon}^{MG}$ for spherical particles is given by,

$$\frac{\bar{\epsilon}^{MG}-\epsilon_m}{\bar{\epsilon}^{MG}+2\epsilon_m} = f\,\frac{\epsilon-\epsilon_m}{\epsilon+2\epsilon_m} \qquad (13)$$

where f is the volume fraction of the metallic phase. The above equation has been generalized further to take into account the size distribution of the spherical particles and the consequent size dependence of the dielectric permeability of the metallic species[54] as follows,

$$\bar{\epsilon}^{MG} = \epsilon_m\,\frac{1 + \frac{2}{3}\sum_j f_j\,\alpha_j}{1 - \frac{1}{3}\sum_j f_j\,\alpha_j} \qquad (14)$$

The subscript j denotes particles having a mean diameter x_j; and the f_j's are a set of fractional filling factors normalized by $\sum_j f_j$. $f_j \propto_j$ is proportional to the polarizability of particles in the jth class and for spheres is given by,

$$\alpha_j = \frac{\varepsilon_j - \varepsilon_m}{\varepsilon_m + \frac{1}{3}(\varepsilon_j - \varepsilon_m)}. \tag{15}$$

The Maxwell–Garnett model is valid only for very small filling factors. A self-consistent effective medium theory which removes this restriction and which has been used extensively in recent years[54,58,59] is the one originally put forward by Bruggeman[60]. The effective dielectric permeability in this model is given by,

$$\bar\varepsilon^{-BR} = \varepsilon_m \frac{1 - f + \frac{1}{3}\sum_j f\,\alpha_j}{1 - f - \frac{2}{3}\sum_j f_j\,\alpha_j}. \tag{16}$$

The above effective medium theories give qualitative agreement with experimental data. The computed results can be brought into fair agreement with the experiments by using suitable values of the plasma frequency for the particles and effective sample thicknesses. Further improvement can be effected by assuming that the samples consist of a mixture of close-packed clusters, infinite linear chains and independent single particles[54]. Electron microscopic data do support existence of such geometrical configurations.

1. Granqvist, C. G. and Buhrman, R. A., *J. Appl. Phys.*, 1976, 47, 2200.
2. Abeles, B., Sheng, P., Coutts, M. D. and Arie, Y., *Adv. Phys.*, 1975, 24, 407.
3. Rawson, H., *Properties and applications of glasses (Glass Science and Technology 3)* Elsevier Publishing Co., Amsterdam. p. 218, 1980.
4. Sinfelt, J. H., *Science*, 1977, 195, 641.
5. Meier, F. and Wyder, P., *Phys. Rev. Lett.*, 1973, 30, 181.
6. Tanner, D. B., Sievers, A. J. and Buhrman, R. A., *Phys. Rev.*, 1975, B11, 1330.

7. Yee, P. and Knight, W. D., *Phys. Rev.*, 1975, B11, 3261.
8. Niklasson, G. A., Granqvist, C. G. and Hunderi, O., *Appl. Opt.*, 1981, 20, 26.
9. Andersson, A., Hunderi, O. and Granqvist, C. G., *J. Appl. Phys.*, 1980, 51, 754.
10. McMillan, P. W., *Glass-Ceramics*, Academic Press, New York, p. 61, 1979.
11. Araujo, R. J., *Photochromic glass in treatise on materials science and technology*, (ed.), M. Tomozawa and R. W. Doremus, Vol. 12, Academic Press, New York, p. 91, 1977.
12. Stookey, S. D., Beall, G. H. and Pierson, J. E., *J. Appl. Phys.*, 1978, 49, 5114.
13. Chopra, K. L., *Thin film phenomena*, McGraw-Hill, New York, p. 329, 1969.
14. Granqvist, C. G., in *Electrical transport and optical properties of inhomogeneous media*, (eds), J. C. Garland and D. B. Tanner, American Institute of Physics, New York, p. 200, 1978.
15. Kazmerski, L. L. and Racine, D. M., *J. Appl. Phys.*, 1975, 46, 791.
16. Neugebauer, C. A., in *Handbook of thin film technology*, (eds) L. I. Maissel and R. Glang, McGraw Hill, New York, p. 32, 1970.
17. Yee, P. and Knight, W. D., *Phys. Rev.*, 1975, B11, 3261.
18. Faure, R., Carlan, A., Crebassa, J., Desrousseaux, G. and Robrieux, B., *Thin Solid Films*, 1972, 9, 329.
19. Skrofronick, J. G. and Phillips, W. B., *J. Appl. Phys.*, 1967, 38, 4791.
20. Zeller, H. R. and Kuse, D., *J. Appl. Phys.*, 1973, 44, 2763.
21. Granqvist, C. G. and Buhrman, R. A., *J. Appl. Phys.*, 1976, 47, 2200.
22. Phalen, R. F., *Aerosol. Sci.*, 1972, 3, 395.
23. Weber, F. N. and Shear, D. D., *J. Appl. Phys.*, 1969, 40, 3854.
24. McBride, D. D. and Sherman, P. M., *AIAA. J.*, 1972, 10, 1058.
25. Fan, J. C. C. and Zavracky, P. M., *Appl. Phys. Lett.*, 1976, 29, 478.
26. Craighead, W. G. and Buhrman, R. A., *Appl. Phys. Lett.*, 1977, 31, 423.
27. Fan, J. C. C. and Spura, S. A., *Appl. Phys. Lett.*, 1977, 30, 511.
28. Svedberg, T., *Kolloid Z.*, 1919, 24, 1.
29. Zsigmondy, R., *Z. Phys.*, 1906, 56, 65.
30. Von Fragstein, C. and Schoenes, F. J., *Z. Phys.*, 1967, 198, 477.
31. Via, G. H., Sinfelt, J. H. and Lytle, F. W., *J. Chem. Phys.*, 1979, 71, 690.
32. McMillan, P. W., *Glass Ceramics*, Academic Press, London, New York, p. 65, 1979.
33. Chakravorty, D., Bandyopadhyay, A. K. and Nagesh, V. K., *J. Phys.*, 1977, D10, 2077.

34. McMillan, P. W., *Phys. Chem. Glasses*, 1976, **17**, 193.
35. Stookey, S. D., Beall, G. H. and Pierson, J. E., *J. Appl. Phys.*, 1978, **49**, 5114.
36. Chakravorty, D., *J. Non-Cryst. Solids*, 1974, **15**, 191.
37. Chakravorty, D., Shuttleworth, A. and Gaskell, P. H., *J. Mater. Sci.*, 1975, **10**, 799.
38. Cohen, M. H., Jortner, J. and Webman, I., *Electrical transport and optical properties of inhomogeneous media*, (eds) J. C. Garland and D. B. Ranner, American Institute of Physics, New York, p. 63, 1978.
39. Abeles, B., Pinch, H. L. and Gittleman, J. I., *Phys. Rev. Lett.*, 1975, **35**, 286.
40. Chakravorty, D., Haranahalli, A. R. and Kumar, D., *Phys. Stat. Sol.*, 1979, **51**, 275.
41. Chakravorty, D. and Chakravarti, S., *J. Non-Cryst. Solids*, 1980, **38** and **39**, 295.
42. Chakravorty, D., Keshavaram, B. N. and Venkateswaran, A., *J. Mater. Sci.*, 1979, **14**, 2991.
43. Chakravorty, D., *Appl. Phys. Lett.*, 1974, **24**, 62.
44. Chakravorty, D. and Murthy, C. S., *J. Phys.*, 1975, **D8**, L162.
45. Das, G. C. and Chakravorty, D., J. Appl. Phys., 1980, **51**, 3896.
46. Das, G. C. and Chakravorty, D., *J. Phys. D.*, 1982, (to be published).
47. Abeles, B., Cohen, R. W. and Cullen, G. W., *Phys. Rev. Lett.*, 1966, **17**, 632.
48. Garland, J. W., Brennemann, K. H. and Mueller, F. M., *Phys. Rev. Lett.*, 1968, **21**, 1315.
49. Klein, J. and Leger, A., *Phys. Lett.*, 1968, **A28**, 134.
50. Rayl, M., Wojtowicz, P. J., Abrahams, M. S., Harvey, R. L. and Biochi, C. J., *Phys. Lett.*, 1971, **A38**, 477.
51. Gittleman, J. I., Goldstein, Y. and BoZowski, S., *Phys. Rev.*, 1972, **B5**, 360.
52. Sheng, P., *Electrical transport and optical properties of inhomogeneous media*, (eds) J. C. Garland and D. B. Tanner, American Institute of Physics, New York, p. 143, 1978.
53. Niklasson, G. A. and Granqvist, C. G., *J. Appl. Phys.*, 1979, **50**, 5500.
54. Granqvist, C. G. and Hunderi, O., *Phys. Rev.*, 1977, **B16**, 3513.
55. Sarkar, P., M.Tech. Thesis, Indian Institute of Technology, Kanpur, 1981.
56. Maxwell-Garnett, J. C., *Phil. Trans. R. Soc. London*, 1904, **203**, 385.
57. Maxwell-Garnett, J. C., *Phil. Trans. R. Soc. London*, 1906, **205**, 237.
58. Elliott, R. J., Krumhansl, J. A. and Leath, P. L., *Rev. Mod. Phys.*, 1974, **46**, 465.
59. Wood, D. M. and Ashcroft, N. W., *Phil. Mag.*, 1977, **35**, 269.
60. Bruggeman, D. A. G., *Ann. Phys. (Leipzig)*, 1935, **24**, 636.