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OSTWALD RIPENING IN IONIC CRYSTALS

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Résumé. — La théorie de Lifshitz-Slezov-Wagner (LSW) *Ostwald Ripening*, limitée par la diffusion en volume ou les taux de réaction en surface, est étendue au cas de la diffusion par les dislocations ou les joints de grain. La théorie prévoit une distribution universelle de taille de particule, $F(R/R_c)$ où R_c est le rayon critique, i. e. le rayon d'une particule qui est instantanément en équilibre avec la concentration en soluté dans la matrice. Quelques-unes des approximations faites dans la théorie sont discutées. L'approximation $e^{\alpha/R} \simeq 1 + \alpha/R$ utilisée en appliquant l'équation de Thomson à la théorie n'est pas toujours valide et peut provoquer une erreur significative dans la forme de la fonction de distribution des tailles pour les faibles valeurs de R . Des inhomogénéités dans la distribution des distances entre particules peuvent provoquer la coalescence indépendante de différents groupes de particules dans le même solide, ce qui donne une distribution de tailles observée en désaccord avec la théorie simple.

Une comparaison de la théorie avec des expériences récentes dans des halogénures alcalins et des verres confirme les résultats précédents et explique de nombreuses observations correctement. La distribution des tailles observée pour des particules d'argent dans le verre est décrite par deux distributions se recourant pour le cas de diffusion en volume. Les particules d'Ag dans KCl sont décrites par la distribution étroite obtenue pour la diffusion par dislocation, et la distribution de $\text{MnCl}_2 \cdot 6 \text{NaCl}$ (phase de Suzuki) dans NaCl par la réaction de surface dans les limites des approximations discutées.

Abstract. — The Lifshitz-Slezov-Wagner (LSW) theory of Ostwald ripening, limited by bulk diffusion or surface reaction rates, is extended to the case of dislocation or grain-boundary diffusion. The theory predicts a universal particle size distribution, $F(R/R_c)$, where R_c is the critical radius i.e. the radius of a particle which is instantaneously in equilibrium with the solute concentration in the matrix. Some of the approximations used in the theory are critically examined. The approximation $e^{\alpha/R} \simeq 1 + \alpha/R$, used in applying Thomson's equation to the theory, is not always valid and can cause a significant error in the shape of the size distribution function for small values of R . Inhomogeneities in the distribution of interparticle separation can cause different groups of particles in the same solid to ripen independently, thus giving an observed size distribution which does not agree with the simple theory.

A comparison of the theory with recent experiments on alkali halides and glass supports the above findings and explains a variety of observations satisfactorily. The observed size distribution of Ag particles in glass is described by two overlapping distributions for the bulk diffusion case. Ag particles in KCl are described by the narrow distribution obtained for the dislocation diffusion case and the distribution of $\text{MnCl}_2 \cdot 6 \text{NaCl}$ (Suzuki phase) in NaCl by the surface reaction case when allowance is made for the errors due to the approximations discussed above.

1. Introduction. — The kinetics of precipitation from a supersaturation of solute atoms or defects in a crystal matrix have been extensively discussed by numerous authors e. g. [1-7], and recently applied to the aggregation of F centres into metallic colloids [8]. The precipitation process proceeds until the supersaturation of solute has become small, and most of the excess solute has been incorporated into precipitated particles. The particle size distribution during this process remains fairly narrow. However, this distribution does not persist, because the larger interfacial energy of a large number of small particles drives the system towards a situation where the mean particle size is increased. This process is known as Ostwald ripening, and in principle extends until the particles

have grown into a single large precipitate or the solute has migrated to the surface of the crystal [9].

The mechanism of Ostwald ripening relies on the transport of solute from small precipitates to larger precipitates, so that the small ones shrink and the large ones grow. These solute currents arise because the solute concentration C_R in equilibrium with a particle of radius R is given by Thomson's equation [9].

$$C_R = C_\infty \exp(\alpha/R). \quad (1)$$

C_∞ is the solute concentration in equilibrium with a plane surface and $\alpha = 2 \Omega \sigma / kT$, where Ω is the atomic volume and σ the interfacial energy of the particle in the matrix. Since C_R is larger for small values of R a concentration gradient will exist so that solute flows from the region near a small particle towards a large particle. During Ostwald ripening a range of particle sizes will be present.

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The theory of Ostwald ripening was formulated by Greenwood [10] and considerably extended by Lifshitz and Slezov [11-12] and Wagner [13]. These theories predict that the ripening system evolves into a quasi steady state in which the size distribution $F(u)$ expressed in terms of the reduced variable $u = R/\bar{R}$ does not change with time and in which the mean radius \bar{R} grows as t^n where $n < 1$. The exponent n is $\frac{1}{2}$ when the ripening process is controlled by the rate at which solute evaporates and condenses at the particles (case 1), and $\frac{1}{3}$ when the rate-limiting process is bulk diffusion of solute atoms (case 2). Extensive experimental work has been done to test these theories in the case of metal alloys [9], with reasonable success. However, the observed size distributions are usually rather wider than predicted. Very little work has been done on ionic crystals and glasses, although size distributions of colloids and precipitates have been reported [14-18], and some attempt has been made to interpret the ripening results theoretically [19-21]. In this paper we report a more extensive analysis of the experimental results, and extend the Lifshitz-Slezov-Wagner (LSW) theory in two important respects. The first of these is to cover the case where transport of solute between particles takes place by dislocation or grain boundary diffusion (case 3) rather than through the bulk crystal. We also show that it is possible under some conditions for different groups of precipitate particles to ripen almost independently in the same crystal. This leads to an interpretation of features of the observed size distributions which are not explained by the conventional LSW theory. Since the detailed arguments have been presented in another report [22] we shall concentrate only on the main results.

2. Ripening theory and its extension to dislocation and grain boundary diffusion. — Suppose that the concentration of solute at a point distant from a precipitate particle is C_a , i. e. C_a represents the average value of the solute concentration in the bulk of the crystal. The rate of change of the radius of a particle is then given in the steady state approximation (see [11, 22]) by

$$\frac{dR}{dt} = \frac{A}{R^n} \frac{(C_a - C_R)}{C_p} \quad (2)$$

where $n = 0, 1$ and 2 for case 1, 2 and 3 respectively and A is a constant factor. C_p is the concentration of solute atoms in the precipitate. The constant A is equal to the surface reaction rate constant K in case 1 [13], the bulk diffusion coefficient D in case 2 [11] and the dislocation or grain boundary transport parameter G in case 3 [22]. G is a function of the bulk and dislocation or grain boundary diffusion coefficients whose precise form depends on the assumptions made in deriving equ. (2) (see [22]). The form of equ. (2) has been used by LSW for cases 1 and 2. For case 3, $n = 2$, has been shown to be approximately true for grain boundaries [9, 22] and for the related problem of

islands growing on a substrate [23, 24]. The extension to dislocation diffusion is made in detail in [22]; the R^{-2} dependence arises simply whenever the solute current to or from a particle is independent of particle size, as it will be for a one dimensional diffusion path.

Using equ. (1) and assuming $\alpha \ll R$ (see later for a discussion of this point) we can write

$$C_R = C_\infty(1 + \alpha/R) \quad (3)$$

which allows equ. (2) (with $A = G$ and $n = 2$) to be written as

$$\frac{dR}{dt} = \frac{G\alpha C_\infty}{C_p R^2} \left(\frac{1}{R_c} - \frac{1}{R} \right) \quad (4)$$

R_c , the *critical radius*, is the radius of a particle which is *instantaneously* in equilibrium with the average solute concentration C_a , i. e. the radius of a particle which is *instantaneously* neither growing nor shrinking. Thus

$$\alpha/R_c = (C_a - C_\infty)/C_\infty. \quad (5)$$

R_c is a crucial parameter in the LSW theory, since the radius distribution function expressed in terms of $u = R/R_c$ is found to be asymptotically independent of the time t at large times such that $R_c \gg R_c(t = 0)$.

Adapting the method of Lifshitz and Slezov [11, 12] to case 3, we find that the size distribution function $f(R, t)$ is given by

$$f(R, t) = \frac{\text{const.}}{t} F_3(u) \quad (6)$$

$F_3(u) =$

$$= \frac{u^3 \exp \left[\frac{-2}{3(u_0 - u)} \right] \exp \left[-\frac{1}{6\sqrt{2}} \tan^{-1} \left(\frac{u + u_0}{u_0 \sqrt{2}} \right) \right]}{(u_0 - u)^{19/6} (u^2 + 2uu_0 + 4u_0^2)^{23/12}} \quad \left. \begin{array}{l} \text{for } u \leq u_0 = 4/3 \\ F_3(u) = 0 \text{ for } u > 4/3. \end{array} \right\} \quad (7)$$

For

$$t \gg \tau_3 = \frac{64 C_p R_c^4(0)}{27 \alpha G C_\infty}$$

we also have

$$R_c^4 = R_c^4(0) (1 + t/\tau_3) \quad (8)$$

$$C_a - C_\infty = \frac{\alpha C_\infty}{R_c} \propto t^{-1/4} \quad (9)$$

and the number of particles $n(t) \propto t^{-3/4}$.

The distribution $F_3(u)$ also applies to the growth of particles on surfaces (cf. [23 and 24]). Corresponding expressions for the other cases 1 and 2 are given in the Appendix. Note that the distribution functions $F(u)$ fall to zero at some upper limit of u , which is 2.0 for case 1, 1.5 for case 2 and 1.33 for case 3. The asymptotic time dependence of R_c is $R_c \propto t^{1/(n+2)}$. Plots of $F_1(u)$, $F_2(u)$ and $F_3(u)$ are shown in figure 1. In all cases $R_c = f\bar{R}$ where $f = 1$ for case 2 and is close to 1

for the other cases. It is also possible to relate R_c exactly to the mean value of some power of R [13, 22]. Thus in case 3, $R_c^{-1} \equiv \overline{R^{-1}}$.

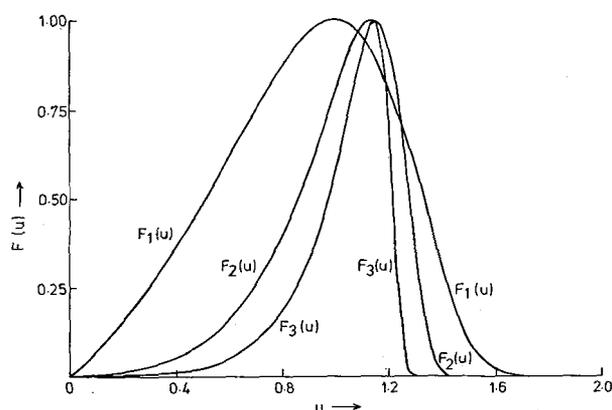


FIG. 1. — Theoretical size distributions: $F_1(u)$ for the surface reaction case, $F_2(u)$ for the bulk diffusion case and $F_3(u)$ for the dislocation and grain boundary diffusion case. The maximum values of the three functions occur at $u = 1.00$, $u = 1.135$ and $u = 1.142$. Note that $F(u)$ varies as u , u^2 and u^3 near $u = 0$ in the three cases.

3. Modifications to the theory for small values of R . — One of the assumptions used in the LSW theory is that $\alpha/R \ll 1$ in equ. (1) so that the exponential can be expanded. This must introduce some error for small values of R , whose effect may be found as follows.

The total number of particles per unit volume $n(t)$ is given by

$$n(t) = \int_0^{\infty} f(R, t) dR \quad (10)$$

and from the equation of continuity

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial R} (f \cdot \dot{R}) = 0 \quad ([11-13])$$

it follows that

$$-\frac{dn}{dt} = -\frac{d}{dt} \int_0^{\infty} f(R, t) dR = -\lim_{R \rightarrow 0} [f(R, t) \dot{R}]. \quad (11)$$

Since dn/dt must depend only on t , it follows that as $R \rightarrow 0$ the function $f(R, t)$ must show the inverse functional dependence on R to \dot{R} . From equ. (2) it then follows that for small R ($\ll R_c$)

$$f(R, t) \propto \frac{R^n}{e^{\alpha/R} - 1} \quad (12)$$

which is to be contrasted with $f(R, t) \propto R^{n+1}$ (i. e. $F_{n+1}(u) \propto u^{n+1}$) which results when equ. (3) is used. The two forms are compared in figure 2. It can be seen that the changes in $f(R, t)$ at small R will be most obvious in case 1.

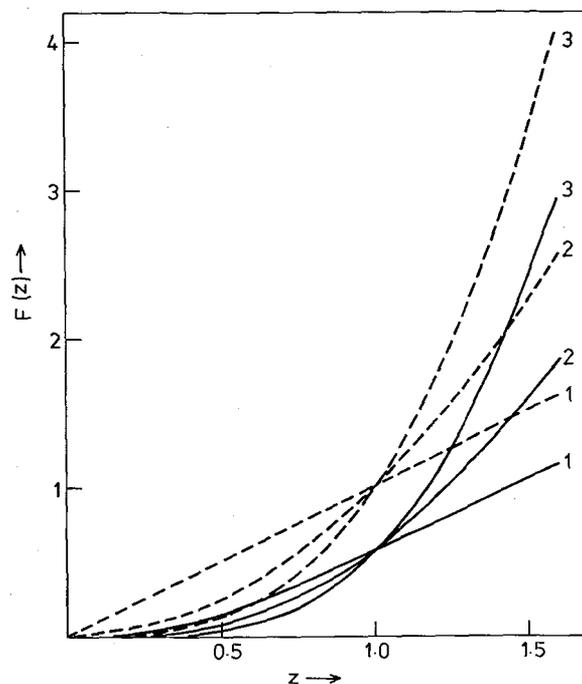


FIG. 2. — Comparison of the functions $F(z) = z^n / (e^{1/z} - 1)$ (full lines) and $F(z) = z^{n+1}$ (dashed lines) for $n = 0, 1$ and 2 as appropriate for cases 1, 2 and 3. The variable z is written for R/α (see text).

Appropriate values of σ to use in equ. (1) are not known with certainty for most systems (see [25 and 26]). Taking a probably high value of $\sigma = 1000$ ergs cm^{-2} , and $\Omega = 5 \times 10^{-23}$ cm^3 , $T = 1000$ K, gives $\alpha = 7$ nm, so that the discrepancy due to using equ. (3) would become significant for $R \lesssim 20$ nm. For very small particles even equ. (1) will cease to be valid since σ becomes size-dependent [27]. One can thus expect that the size distributions observed experimentally may deviate somewhat from the curves in figure 1 for small values of u .

4. The effect of inhomogeneities on ripening. — It seems intuitively possible that if two or more groups of particles are formed well-separated from one another in the crystal, then each group may approximate closely to an LSW system and ripen almost independently, with the values of C_a (and hence R_c) continuing to be different in each region. This possibility is suggested by some of the electron microscope studies of precipitates (e. g. [18, 28]) which tend to show groups of particles in a very inhomogeneous spatial distribution. We may examine this situation more quantitatively by comparing the value of $(dC_a/dt)_r$ due to ripening within each LSW system with the rate $(dC_a/dt)_i$ at which C_a in each region tends to change due to inter-region diffusion. If

$$(dC_a/dt)_i \ll (dC_a/dt)_r$$

then we would conclude that each region will ripen independently without communicating with other regions. We shall examine this condition initially for the specific example of case 2 i. e. bulk diffusion.

From equ. (A7) of the Appendix it follows that

$$\left| \left(\frac{dC_a(1)}{dt} \right)_r \right| = \frac{4 \alpha^2 C_\infty^2 D}{27 C_p R_c^4(1)} \quad (13)$$

where $R_c(1)$ refers to region 1 etc. For a diffusion process we can write

$$\left| \left(\frac{d}{dt} [C_a(2) - C_a(1)] \right)_i \right| \sim \frac{D}{L^2} [C_a(2) - C_a(1)] \\ = \frac{D \alpha C_\infty}{L^2} \left[\frac{1}{R_c(2)} - \frac{1}{R_c(1)} \right] \quad (14)$$

where L is the distance separating region 1 and region 2. The condition for independent ripening regions thus becomes

$$\frac{\alpha}{R_c^3(1)} \cdot \frac{C_\infty}{C_p} \gg \left| \frac{1}{L^2} \left(\frac{1}{\beta} - 1 \right) \right| \quad (15)$$

with $R_c(2) = \beta R_c(1)$. If two systems are to be recognized as ripening independently, then $R_c(2)$ must be significantly different from $R_c(1)$ i. e. β appreciably greater or less than unity. Equ. (15) shows that if $\beta \sim 0.5$ the condition for independent ripening is not difficult to satisfy. For example, if $\alpha/R_c \sim 0.3$ and $C_p/C_\infty \sim 10^3$ we have $(L/R_c)^2 \gg 3 \times 10^3$ i. e. $L \gg 50 R_c$. Thus if $R_c \sim 20$ nm the two regions need only be separated by several microns. We may thus conclude that it is very likely that in a relatively dilute system there may be several groups of particles ripening almost independently. Experimental size distributions would then be superpositions of several different distribution functions with different values of R_c . The arguments are easily extended to cases 1 and 3. It turns out that the condition becomes easier to satisfy as one progresses from case 1 through case 2 (as above) to case 3. The existence of independent groups with different values of R_c presupposes, of course, that the different regions have reached different stages of the precipitation and ripening process at a given time. This does not seem unreasonable where inhomogeneous nucleation (e. g. on dislocations) is involved. Finally, it should be remembered that equ. (2) applies only when one of the three solute transport processes is truly rate-limiting. In the general case where more than one process must be taken into account the expression for dR/dt becomes intermediate between the simple cases [9, 13]. Size distribution functions have not been worked out under these circumstances, but presumably they are intermediate between those shown in figure 1.

5. Comparison of the theory with experiments. —

5.1 SILVER PARTICLES IN GLASS. — Kreibig [15] has produced silver particles in photosensitive glass containing 0.02-0.06 % of Ag_2O . Efforts have been made to fit each of the theoretical curves in figure 1 with the size distribution as measured by Kreibig. The fits were made by adjusting the scale of the radius

coordinate so that the peak of the theoretical curve comes close to that of the experimental histogram. Using this procedure various fits can be tried and judged independently. As shown in figure 3, $F_1(u)$ is too broad to give a satisfactory fit to the data, regardless of variations in fitting procedure. On the other hand, both the curves $F_2(u)$ and $F_3(u)$ are much too narrow when compared with the observed distribution. In any case one would not expect the dislocation or grain boundary case to be relevant for a glass.

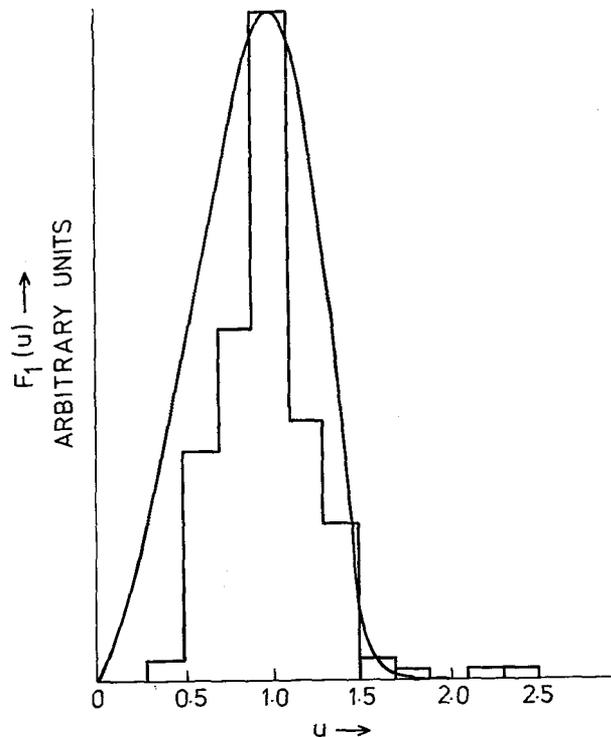


FIG. 3. — A comparison of the theoretical size distribution function $F_1(u)$ with the experimental data for silver particles in glass obtained by Kreibig. The experimental data have been recast in terms of $u = R/R_c$ by choosing a value of R_c which gives the best visual fit.

We suggested in section 4 that all particles need not necessarily form part of one LSW system. Based on this suggestion we have tried and fitted successfully two $F_2(u)$ curves with the observed distribution, the values of \bar{R} being $\bar{R}_1 = 5.0$ nm and $\bar{R}_2 = 6.5$ nm respectively for the two systems. It is seen from figure 4 that the curve $F = F_2(u_1) + F_2(u_2)$ ($u_1 = R/\bar{R}_1$ and $u_2 = R/\bar{R}_2$) agrees well with the observations.

Although this agreement of the sum of two $F_2(u)$ curves with observations supports the suggestion that two or more LSW ripening groups occur independently in many cases, the real test of this suggestion would lie in the measurement of the interparticle distances and radius distributions in the sample. Unfortunately such information is not available in any of the size distribution measurements reported in the literature.

It is seen in figure 4 that there are a few very large particles ($R \sim 10-13$ nm) present in the system with a gap near $R \sim 11.5$ nm where there are no particles.

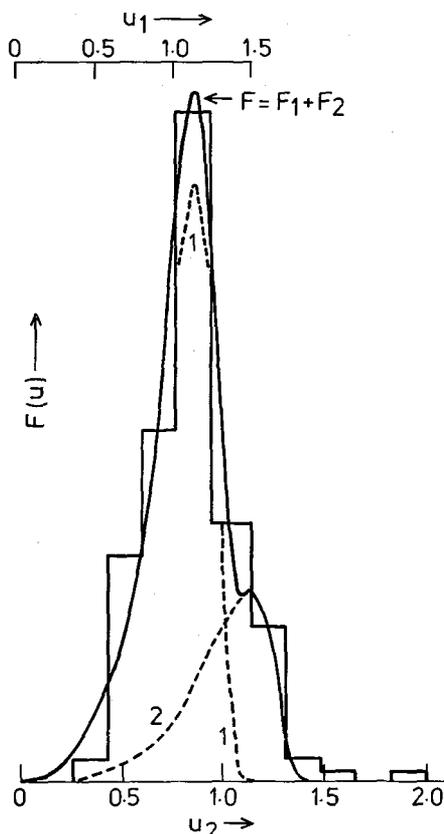


FIG. 4. — Evidence of two LSW systems of silver particles ripening independently in experiments made by Kreibitz. The observed size distribution, shown by histograms, fits with the composite curve $F = F_1 + F_2$ where $F_1 = F_2(u_1)$ and $F_2 = F_2(u_2)$.

We will discuss briefly these large particles along with the results of Shvarts *et al.* [14] and Chassagne [18], in section 6.

5.2 SILVER PARTICLES IN KCl. — Recently Jain and Arora [16] have measured the size distribution of silver particles in KCl. The observed distributions for a crystal ripened for two different times are shown by the histograms in figures 5a and 5b. The distributions

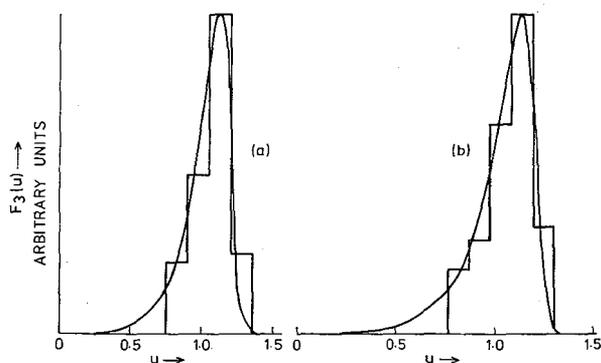


FIG. 5. — Ostwald ripening of silver particles in KCl by diffusion through dislocations observed by Jain and Arora. The observed distributions are perhaps the narrowest reported in the literature and can be fitted only with the sharp theoretical curves $F_3(u)$ obtained for ripening by diffusion through dislocations. $2\bar{R} = 33$ nm for figure 5a and 46 nm for 5b.

are the narrowest of all the measured distributions on different systems that we have seen so far (cf. data in [9 and 29]). The theoretical plot of $F_3(u)$ appropriate for diffusion through dislocations fits extremely well with the observations in both cases as shown in figure 5. Since the ripening was done at a rather high temperature (700 °C), the result that the diffusion is almost completely controlled by transport through dislocations may appear surprising. However, the crystals were grown from the melt, quenched from high temperatures several times and contained a very high dislocation density. Durand *et al.* [8] have also found that metallic colloids are formed by migration of F centres to dislocations even if the alkali halide crystals are not deformed. The most convincing evidence that the colloids are in fact formed at dislocations, even in undeformed crystals, is provided by the direct observations of colloids in the electron microscope [28].

Calleja and Agulló-López [20] have attempted to fit these data using the bulk diffusion distribution $F_2(u)$. They obtain an apparently good fit by superposing the two experimental distributions in figures 5a and 5b, assuming that the $t^{1/3}$ law holds for $\bar{R}(\equiv R_c)$. This superposition, however, results in a distribution which is substantially wider than each separate experimental histogram, and explains why they are able to get a good fit to $F_2(u)$. In fact the ripening times quoted by Jain and Arora are not known precisely enough to test the time dependence of R_c , and the limited data fits neither $t^{1/3}$ nor $t^{1/4}$.

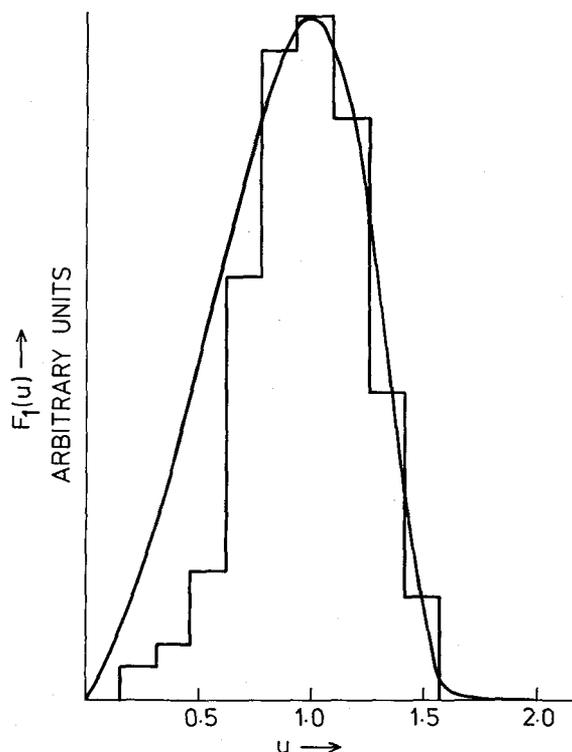


FIG. 6. — Size distribution of the Suzuki phase of $\text{MnCl}_2 \cdot 6\text{NaCl}$ in NaCl crystals observed by Kirk *et al.* (histogram) and theoretical plot of $F_1(u)$, the LSW curve for surface controlled reaction for $\bar{R} = 128$ nm.

5.3 SUZUKI PHASE IN NaCl. — Kirk, Khan and Pratt [17] have studied precipitates of the Suzuki phase $\text{MnCl}_2 : 6 \text{ NaCl}$ in Mn doped NaCl crystals. The size distribution of the precipitates measured by them in a crystal containing 225 ppm of MnCl_2 is shown in figure 6.

A study of the Suzuki structure shows that both Mn^{2+} and its charge compensating cation vacancy have to be incorporated in the precipitate at specific locations. It is therefore likely that a relatively slow surface reaction will control the growth kinetics and we compare the theoretical distribution $F_1(u)$ with the experimental results in figure 6. The agreement of theory with experiment is good except for the very small number of particles for $u < 0.5$. This discrepancy is perhaps to be expected in view of the discussion of the approximation used in expanding Thomson's equation in section 3. It was mentioned earlier that this error is expected to be most apparent in the surface reaction case 1. The experimental distribution is too wide to be fitted satisfactorily by either $F_2(u)$ or $F_3(u)$, although it could probably be fitted by a superposition of several such curves.

6. The presence of large particles and the influence of gross inhomogeneities. — We have seen in section 5 that there were a few large particles of silver present in the glass in Kreibig's experiments. These did not form part of the two LSW systems which described the size distribution of the rest of the particles. The occurrence of these anomalously large particles is not unique to silver particles in glass and is found in many other systems [17, 29]. Shvarts *et al.* [14] have reported the size distribution of Na and K colloids in heavily coloured NaCl and KCl. They found that the distribution of colloids was highly inhomogeneous in their crystals, and a long tail is observed on the large size side of the size distribution. The size distribution spectra of Chassagne [18] are also very complex and show an anomalously large population of large particles. A notable result of the LSW theory for Ostwald ripening is the sharp cut-off at some value of R close to but larger than \bar{R} on the large size side. The presence of a few very large particles or a gradual tail on the large size side are results exactly opposite to the predictions of the theory.

A close study of the results of Shvarts *et al.* [14] and Chassagne [18] shows that the distribution of particles in space in the crystals is characterized by large inhomogeneities. In many of the photographs of colloids in crystals [18] the spacing between the surfaces of the colloidal particles is less than the particle radii R . These features suggest that in these systems we are dealing with conditions which result in at least some of the colloidal particles being too close together to meet the criteria for the applicability of the LSW theory, since the concepts of steady state diffusion and symmetry around each particle which are used to derive equ. (2) break down. A satisfactory theory of Ostwald ripening under these conditions is not available (see however [29] and references therein for an attempt at the problem). In addition, it is also possible that very closely spaced particles may coalesce by actual particle migration (driven in the case of colloids presumably by surface diffusion). This effect is not included in the main results of the LSW theory of ripening, but is extremely important for the growth of particles in vapours and liquids where it is the dominant ripening process (see for example [30-34]).

Despite these difficulties, we can understand in a general way the features of the size distribution for systems where some particles are formed very close together. Such a cluster of closely spaced particles can ripen independently of the behaviour of the rest of the particles in the solid, so that it may ripen relatively quickly into one large particle. If there are several such clusters of particles, the situation after some period of ripening may be that of a few very large particles originating from these clusters, plus the rest of the solid which may still contain one or more groups of more dispersed particles which are still forming LSW systems. In any one experiment, the particle size distribution is then likely to display evidence for an LSW-type distribution plus some anomalously large particles.

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Appendix. — Ripening theory results for case 1 ($n = 0$) and case 2 ($n = 1$).

CASE 1.

$$F_1(u) = \frac{u \exp \left[\frac{-3u}{2-u} \right]}{(2-u)^5} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{(A1)}$$

for $u \leq 2.0$

$$F_1(u) = 0 \text{ for } u > 2.0$$

$$\text{For } t \gg \tau_1 = \frac{2 C_p R_c^2(0)}{\alpha K C_\infty} :$$

$$R_c^2 = R_c^2(0) (1 + t/\tau_1) \quad \text{(A2)}$$

$$C_a - C_\infty \propto t^{-1/2} \quad \text{(A3)}$$

$$n(t) \propto t^{-3/2} . \quad \text{(A4)}$$

CASE 2.

$$F_2(u) = \frac{u^2 \exp \left[\frac{-2u}{3-2u} \right]}{(3+u)^{7/3} (3-2u)^{11/3}} \quad \text{(A5)}$$

for $u \leq 1.5$

$$F_2(u) = 0 \text{ for } u > 1.5$$

$$\text{For } t \gg \tau_2 = \frac{9 C_p R_c^3(0)}{4 \alpha D C_\infty} :$$

$$R_c^3 = R_c^3(0) (1 + t/\tau_2) \quad \text{(A6)}$$

$$C_a - C_\infty \propto t^{-1/3} \quad \text{(A7)}$$

$$n(t) \propto t^{-1} . \quad \text{(A8)}$$

DISCUSSION

A. B. LIDIARD. — You said it was reasonable that the precipitation of Ag in glass should be described by two independent distributions because electron microscope observations showed spatial distributions not to be homogeneous. Have you any idea why this should be ?

A. E. HUGHES. — Inhomogeneous spatial distributions are likely to arise if the initial precipitation process takes place under conditions which are not ideal : e. g. if there are temperature gradients or residual stresses in the material.