Small-Angle Scattering Studies of Phase Separation and Defects in Inorganic Materials

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Abstract

The use of X-ray and neutron small-angle scattering in the study of microstructural changes in inorganic materials is reviewed, with emphasis on recent developments. In the kinetics of diffusion-controlled phase separation, reliable data on the evolution of size and shape of the decomposition products may be obtained especially from in situ ageing experiments. Magnetic neutron scattering is discussed for inhomogeneous ferromagnets. While for the structural characterization of binary systems single-wavelength experiments are sufficient, variable X-ray wavelengths now available at synchrotron-radiation facilities open possibilities for the study of partial structure functions in systems containing several components. The combined use of small-angle scattering and complementary techniques is of particular value in more complex cases. These points are illustrated by a survey of recent results on phase separation and precipitates in binary and ternary crystalline alloys and on radiation-induced microstructural changes in metallic and semiconducting materials.

1. Introduction

Small-angle scattering (SAS) of neutrons (SANS) and of X-rays (SAXS) is ideally suited for the study of inhomogeneities in condensed matter on a length scale from a few interatomic distances to about 1 μm. In many inorganic materials, positional or compositional disorder, clusters and agglomerates of solute atoms and other point defects, finely dispersed phases, fluctuations and modulations in density, concentration or magnetization are decisive for the macroscopic properties. Often, the most desirable properties correspond to a state far from thermodynamic equilibrium. It is therefore not only necessary to characterize a particular microstructure but also to understand the kinetic aspects of its development with time and temperature.

As the SAS amplitude is controlled by locally averaged changes in the scattering-length density (for X-rays this is the effective electron density multiplied by the classical electron radius, for neutrons the nuclear or magnetic scattering-length density), but the measured intensities are a function of density-density correlations, different objects in real space may lead to the same SAS function. More direct information obtainable from transmission electron, field ion or scanning tunnelling microscopy is often necessary to distinguish between different microstructural models. Within these limitations, SAS techniques nevertheless have been instrumental in many studies of microstructural features in inorganic materials. The theoretical foundations for the case of X-rays (Guinier & Fournet, 1955; Gerold, 1967) can be extended to SANS (Schmatz, 1973; Kostorz, 1979, 1983a), and reviews of applications to inorganic materials have been published on numerous occasions [Schmatz (1973, 1978); Gerold & Kostorz (1978); Kostorz (1979, 1982, 1983a,b, 1988a,b); for ceramics see Page (1988); for vitreous and amorphous systems see Wright (1985); Lamparter & Steeb (1988); Kranold & Walter (1991)]. In view of these publications and the other pertinent contributions at this conference, the present survey will concentrate on recent work concerning (mostly diffusion-controlled) decomposition of crystalline alloys, magnetic SANS and defects in alloys and semiconductors.

2. Phase separation and precipitates in alloys

The formation of new phases, often on a very fine scale, from an initially homogenized state quenched from a higher temperature or by other non-equilibrium techniques, is a frequent event in the heat treatment of alloys. The reverse process ('reversion') may also be of interest [see Okuda, Osamura, Hashizume & Amemiya (1988) for a SAXS study of reversion in Al–Zn]. Diffusion-controlled transformations may be frozen in at various stages and subsequently studied by SAS or, if reactions proceed on the appropriate time scale, kinetic studies may be performed in situ. The field of phase separation has received considerable attention owing to the rapid theoretical and numerical developments concerning the evolution of thermodynamically unstable systems. Various models and methods have been used to derive, among other features, scattering func-
tions for different situations and stages of phase decomposition in statistically isotropic binary systems [for reviews see e.g. Gunton, San Miguel & Sahni (1983); Furukawa (1985); Binder (1984, 1987, 1991)].

2.1. Scaling analysis

Special attention has been given to the self-similarity of the SAS function \( I(Q,t) \) (we use \( I \) for simplicity – with proper calibration, it will correspond to the differential scattering cross section). If a single characteristic length \( L(t) \) controls the evaluation of a decomposing system, \( I(Q,t) \) may be scaled according to

\[
\frac{I(Q,t)}{\bar{I}(t)} = L^3(t) s[Q L(t),t]
\]

where \( t \) is time, \( Q \) is the modulus of the scattering vector \( Q = 4\pi\sin\theta/\lambda \) with \( \lambda \) = wavelength of the incident radiation, \( \theta = \) half the scattering angle, and \( \bar{I} \) is the integrated intensity given by

\[
2\pi^2\bar{I} = \int_0^\infty Q^2 I(Q) dQ.
\]

Scaling is said to hold if the scaled scattering (or ‘structure’) function \( s(QL) \) is independent of time, its detailed shape being typical for the type of reaction. For \( L(t) \), different parameters are used but should (in the case of scaling) not yield different results, e.g. the radius of gyration, \( R_g \), obtained from a Guinier plot, or \( L_m = Q_m^{-1} \) where \( Q_m \) is the \( Q \) value of a (frequently occurring) peak in the SAS curve, or \( L_1 = M_1^{-1} \) where \( M_1 \) is the first moment of \( I(Q) \), i.e.

\[
M_1 = \int_0^\infty Q I(Q) dQ/\int I(Q) dQ.
\]

It is now customary to present a scaling analysis of SAS results on this basis. Power laws for \( Q_m(t) \) and \( I_m(t) = I(Q_m(t)) \) of the form

\[
Q_m(t) = A t^{-a}, \quad I_m(t) = B t^b
\]

with constants \( A, B \) and constant exponents, \( a, b \) are also frequently tested and compared with theoretical results [\( b = 3a \) for scaling, cf. (1), if \( \bar{I} \) is constant].

Available results on polycrystalline alloys have been analysed from different points of view (Simon, Guyot & Lyon, 1988; Kostorz, 1988a,b; Fratzl & Lebowitz, 1989; Binder, 1991). Scaling is usually observed only for advanced stages of decomposition, for dilute as well as for more concentrated systems. The scaled structure function depends on the volume fraction and on the morphology of the decomposition product. There is agreement that in the dilute ‘droplet’ region, i.e. for isolated precipitates, the exponents \( a, b \) in (3) coincide with those already predicted by Lifshitz & Slyosov (1961) and Wagner (1961) if the only remaining driving force is the interfacial energy between precipitate and matrix (\( b = 3a = 1 \)), i.e. no elastic interactions between particles and no shape changes occur. A \( t^{1/3} \) growth law is also occasionally observed for advanced stages in more concentrated systems, e.g. in Al–22 at.% Zn–0.1 at.% Mg (Forouhi & de Fontaine, 1987) and Fe–Cr (Katano & Iizumi, 1984), although several theoretical calculations predict a larger exponent. As an example for a late-time behaviour, Fig. 1 shows the scaled structure function \( s(Q/Q_m) \) for Al–22 at.% Zn–0.1 at.% Mg. Although scaling seems to hold fairly well concerning the main features, and the authors are able to fit an empirically modified function based on the excluded-volume concept (Walker & Guinier, 1953; Rikvold & Gunton, 1982) to the experimental data, a systematic increase with ageing time for \( Q/Q_m \geq 1.5 \) (see Fig. 1) is apparent and, according to the authors, may be attributed to the widening of the miscibility gap as the growing (metastable) precipitates start losing coherency with the matrix. The late-time model has recently been extended (see Fig. 2) (Hoyt & de Fontaine, 1989) and

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Fig. 1. Scaled structure function \( s(Q/Q_m(t)) \) for Al–22 at.% Zn–0.1 at.% Mg ageing at 398 K (late-time behaviour) according to Forouhi & de Fontaine (1987). Ageing times are given in minutes.

Fig. 2. Schematic representation of a collection of spherical precipitates of radius \( R \) and scattering-length density \( p_s \) embedded in a matrix of scattering-length density \( p_m \), leading to the \( p(r) \) function shown in the lower part. From Hoyt & de Fontaine (1989).
compared with experimental results (Hoyt, Clark, de Fontaine, Simon & Lyon, 1989) on Al–12, –22 and –32 at.% Zn studied in situ using synchrotron radiation as well as with several other published results. The half-width of the SAXS maximum varies with the volume fraction of the precipitate phase. Fig. 3 shows a comparison of some experimental results with the width of three model functions. Komura, Takeda, Osamura & Okuda (1988) report a width of about 2.3 for a volume fraction of 2.8% in Al–4 at.% Zn–0.1 at.% Mg (aged at 313 K). The Al–8.0, –10.7 at.% Li alloys investigated by Blaschko, Glas & Weinzierl (1990) at temperatures from 373 to 453 K show scaling even for very small precipitate sizes, independent of temperature for both concentrations, and also a narrower width of $s(LQ)$ for the larger volume fraction. The mismatch of Al$_3$Li in the Al matrix is very small, and this may be a system where the interfacial energy term becomes effective even while the matrix is still supersaturated. Under these conditions, the system may follow stable trajectories in $(L,C)$ space where $L$ is the scaling parameter and $C$ is the volume fraction (Fratzl & Blaschko, 1987) and scaling holds even for a changing integrated intensity. A growth rate proportional to $t^{1/2}$ has been observed in all investigations on Al–Li, essentially without any incubation time (Blaschko et al., 1990 and earlier work quoted therein; Pike, Messoloras & Stewart, 1989; Abis, Caciuffo, Carsughi, Coppola, Magnani, Rustichelli & Stefanon, 1990). For an Al–10.7 at.% Li alloy aged at 463 K, Abis et al. (1990) find coarsening with an essentially constant volume fraction of about 24% and particle growth proportional to $t^{1/3}$. In the two-phase model including interparticle interference, these authors determine a size-distribution function for spherical particles by fitting a linear combination of cubic splines to reproduce the scattering curves for $Q > Q_m$ (Magnani, Puliti & Stefanon, 1988). By varying experimental points within the experimental error and repeating the procedure about fifty times, an error band for the size-distribution function is obtained. The distribution function is then used to extract an interparticle interference function. The shape and width of the particle-size-distribution function differ from those expected for dilute systems. This is attributed to diffusion interaction effects between particles. A scaling analysis shows scaling only for $t > 24$ h, using $M^{-1}$ as the length scale.

### 2.2. Early stages of decomposition

While some 'universal' scaling behaviour may have some meaning for simple metallic systems in the advanced stages of ageing, it is not surprising that such concepts usually break down in the early stages.

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**Fig. 3.** The full width at half-maximum (FWHM) of the scaled structure function is the volume fraction for several theories and experiments. RG: Rikvold & Gunton (1982); TEK: Tokuyama, Enomoto & Kawasaki (1987); HF: Hoyt & de Fontaine (1989); FL: Fratzl & Lebowitz (1989); Pt: $40$ at.% Au (Singhal, Herman & Kostorz, 1978); Al–5.3, –6.8 at.% Zn (Hennion, Ronzaud & Guyot, 1982); Al–6–8, –10 at.% Zn(Mg) (Komura, Osamura, Fuji & Takeda, 1985); Al–12–1 at.% Zn (Guyot & Simon, 1982); Al–22 at.% Zn(Mg) (Forouhi & de Fontaine, 1987; Al–12, –22, –32 at.% Zn (Hoyt et al., 1989); Al–4, –6.8 at.% Zn(Mg) (Komura, Takeda, Osamura & Okuda, 1988); Cu–33 at.% Mn (Gaulin, Spooner & Morii, 1987); Fe–34 at.% Cr (Katano & Iizumi, 1984); Al–Li (see Hoyt & de Fontaine, 1989).

**Fig. 4.** Small-angle-scattering pattern for an Al–6.8 at.% Zn single crystal with (110) faces perpendicular to the incident beam. The other crystallographic orientations are indicated. The crystal was aged in situ at room temperature for (a) 2 h and (b) 7.5 h. The azimuthal dependence of the maximum intensity is visible.
where several properties specific for the particular system (or even - e.g. after quenching - for the particular sample) may influence the kinetics and the scattering function. Even the well-known Al–Zn system is not a very simple case. In Fig. 1 there are details in the scaled structure function attributed to the loss of coherency. But even the coherent precipitates are not always spherical, i.e. the isotropy required for a comparison with currently available theoretical models is not present but brought about by using polycrystals. Fig. 4 (Kostorz, 1982, 1983b) illustrates that SAS measurements on single crystals reveal many details that will be averaged out for a polycrystalline sample. In Fig. 4(a), the average radius of the Guinier–Preston zones is about 1-6 nm, based on a model calculation including a size distribution (Bubeck, Gerold & Kostorz, 1985). The scattering at larger Q shows that the particles are spherical. Nevertheless, the 'isotropic' interference ring found for polycrystals now shows a marked azimuthal variation of the peak intensity indicating some preferred alignment of the zones along (100).

In Fig. 4(b), the peak position has moved to smaller Q values and the average zone radius is now about 2.2 nm. The more rectangular shape of the isointensity lines at larger Q is due to the well known fact (Merz & Gerold, 1966) that zones exceeding a certain size transform from spherical to oblate ellipsoidal shape with the short axis along (111). From these experiments (Bubeck et al., 1985), the critical radius is 1.7 to 2.2 nm. [Model clusters calculated using short-range-order parameters obtained from the evaluation of wide-angle diffuse X-ray scattering experiments (Haeffner & Cohen, 1989) suggest a somewhat smaller critical radius of 1 to 1.3 nm at 353 K.] Shape change and long-range correlations along (100) in Al–Zn are both primarily due to the elastic misfit energy for coherent precipitates. A measure for this misfit is the relative lattice-parameter change with concentration, \( \delta = d \ln a/dc \), in the solubility region. For Al–Zn (\( \delta = -1.9\% \)), this is a moderate but obviously non-negligible contribution which becomes effective in the earliest observable stages (a few minutes with SANS). Recently, Osamura, Okuda, Amemiya & Hashizume (1988) have studied the growth of Guinier–Preston zones in Al–4.0, –6.7, –10 at.\% Zn polycrystals with much better time resolution (0.2 to 10 s), by in situ SAXS, using synchrotron radiation, with new results for early ageing stages at 277/293 K, including in particular the influence of quenching from different temperatures. In an initial stage, the particles which apparently have a diffuse interface [also seen by Haeffner & Cohen (1989) in their simulations], grow proportional to \( t^a \) with \( a = 0.44...0.5 \) (a simple diffusion-controlled growth law would lead to \( a = 0.5 \)) while the integrated intensity still increases dramatically. Fig. 5 shows the radius of gyration as a function of ageing time for one set of alloys. The half-time for the completion of supersaturation-driven decomposition depends exponentially on the quenching temperature, with an apparent activation energy of 0.68 eV which is similar to published vacancy formation energies. If all vacancies are retained during the quench and atomic diffusion in these early stages of decomposition is the dominant mechanism, this is expected. It would be interesting to study single crystals, too, where the density of vacancy sinks is much smaller (which would lead to an increased half-time) and the elastic interactions could be studied in even less-advanced stages.

Single crystals have been studied with similar resolution in the case of dilute Al–Cu (Sato, Murakami, Amamiya, Hashizume & Takahashi, 1988), a system (\( \delta = -12.6\% \)) where the initial coherent decomposition products are flat Cu-rich zones in \{100\} (Guinier–Preston I zones). This experiment was performed to decide whether the GPI zones are monolayers as suggested, for example, by diffuse neutron scattering (Müller, Schönfeld, Kostorz & Bührer, 1989 and references therein) or multilayers, as concluded from X-ray diffuse scattering (Matsubara & Cohen, 1985 and references therein). Although Fig. 6 shows a dramatic increase of the SAXS intensity along [100], indicating that the scattering objects are very thin perpendicular to this direction, Haeffner, Winholtz & Cohen (1988) clearly demonstrate that it is not possible to distinguish between mono- and multilayers on \{100\} from these measurements alone.

If supersaturated Ni–Ti alloys (\( \delta = +9.5\% \)) are aged at intermediate temperatures, a metastable ordered phase with the \( L1_2 \) structure (\( \gamma' \) phase, expected composition Ni\(_3\)Ti), coherent with the matrix, forms first (Ni\(_3\)Ti with \( D0_{21} \) structure is the stable stoichiometric precipitate). At least for certain

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**Diagram**:Radius of gyration for three Al–Zn alloys (○: 4.0 at.%; ●: 6.7 at.%; Δ: 10 at. % Zn) as a function of ageing time at 293 K after quenching from 593 K (from Osamura et al., 1988).
concentrations and ageing temperatures, ordering and phase separation occur simultaneously (see Cerri, Kostorz, Schmelczer, Schönfeld & Schwander, 1988 and references cited therein). Because of the negative neutron scattering length of Ti, SANS is very sensitive to compositional changes and an in situ SANS study (Cerri, Schönfeld & Kostorz, 1990) on Ni–10.5/11.5 at.% Ti single crystals ageing at 773–853 K revealed very early stages of decomposition. Fig. 7 shows scaled presentations of the ageing sequence at 853 K, for appropriately averaged SANS intensities, using three different scaling parameters. Although one of the graphs (using $M^{-1}$) may lead one to conclude that scaling holds, the other presentations show that this may be an artefact. The exponent $\alpha$ in a power law $L \propto t^\alpha$ is about 0.2, much smaller than expected for coarsening, although the integrated intensity seems to reach a plateau after about 250 min. Looking at the two-dimensional

SANS pattern for (100) along the incident beam, it is clearly seen that the coherent scattering objects assume nonspherical shape very early and that a strong interference peak appears along the cubic axes, with strongly decreasing half-width as the ageing time increases. It is likely that coherency strains are very effective in controlling this metastable microstructure. The evaluation of the integrated intensity yields a Ti concentration of $16\pm 3$ at.%, much smaller than expected. Longer ageing sequences will have to be studied in order to determine whether the state reached at 853 K after about 7 h is a transitional one possibly followed by a further Ti enrichment of the $\gamma'$ phase, which may occur if the coherency is partially lost.

In Ni–Al, $\gamma'$ is the stable precipitate phase forming from the supersaturated solid solution. The misfit parameter $\delta$ is about 5%, sufficient to introduce shape changes of the initially spherical particles and a strong anisotropy of the SANS pattern of single crystals (Beddoe, Haasen & Kostorz, 1984; see also Kostorz, 1988c). The mismatch between $\gamma'$ and the $\gamma$ matrix can be reduced by the addition of Mo, with dramatic effects on the growth rate and particle morphology, as shown in an electron microscopy study on larger particles by Conley, Fine & Weertman (1989). An in situ SANS study on single crystals shows a $t^{1/3}$ growth law from the beginning and also with a drastically reduced slope for $dR^3/dt$ when the mismatch is reduced (see Fig. 8). This reduction of the coarsening rate cannot be explained by a difference in undercooling conditions. Furthermore, the particles remain spherical at all times for zero mismatch and the anisotropy, i.e. the difference of the SANS intensity at the peak along (100) and (111) vanishes (Calderon & Kostorz, 1990).
These few examples show how SAS measurements have contributed towards a clear characterization of the influence of interfacial stresses and long-range stress interactions on the kinetics of decomposition. Interfacial stresses (Cahn & Larché, 1982; Cahn, 1989) affect the interfacial energy term, while the interparticle coherency stress interaction is controlled by the misfit and the difference in elastic constants between particle and matrix. For a recent treatment of two-particle stress interactions in an anisotropic crystal, see Johnson, Abinandanan & Voorhees (1990).

For Al–Ag, δ is very small (±0.03%) and coherency strain effects are expected to be negligible. A recent SAXS study on Al–0.3, –3, –5 at. % Ag single crystals shows that the Guinier–Preston zones, even in the earliest stages of decomposition, are not spherical (Dubey, 1990; Dubey, Schönfeld & Kostorz, 1991). The SAXS patterns taken with a two-dimensional position-sensitive detector are best described with a single-particle scattering function for spheres faceted mainly along (111) planes. This is a case where the anisotropy of the interfacial energy is clearly revealed [see also Gragg & Cohen (1971) and Alexander, LeGoues, Aaronson & Laughlin (1984)].

### 2.3. Ternary alloys

In a disordered system with n components, there are n(n + 1)/2 independent partial scattering functions. For substitutional solid solutions, this number is reduced to n(n – 1)/2, i.e. at least three measurements are necessary to determine the distribution of the components in a ternary alloy. During decomposition, the evolution of low- and high-concentration regions may follow a pseudobinary path, i.e. along the tie line connecting the initial and the final states. In this case, the three independent partial functions are proportional to each other. The SAS intensity for spheres faceted mainly along (111) planes. This is a case where the anisotropy of the interfacial energy is clearly revealed [see also Gragg & Cohen (1971) and Alexander, LeGoues, Aaronson & Laughlin (1984)].

For Cu–42 at. % Ni–15 at. % Fe aged at temperatures between 733 and 823 K, anomalous SAXS experiments have shown deviations from a quasibinary behaviour (Lyon & Simon, 1987, 1988). Although the partial structure functions $S_{ij}$ all look very similar, the peak position, $Q_m$ for $S_{CuCn}$ clearly appears at smaller values than $Q_m$ for $S_{NINi}$ or $S_{FeFe}$ and $S_{FeNi}$ is not equal to $S_{FeFe}S_{NiNi}$ – there are thus two independent structure functions in this system. By analysing the deviations from the closest two-phase model structure function, the authors suggest an Ni/Fe segregation layer around the Ni–Fe-rich core of the precipitating phase, which may arise from differences in the mobility of Ni and Fe. While the Cu distribution is homogeneous in both phases, the Ni/Fe concentration profile thus varies over a larger range. With this assumption, the partial structure

\[ I(Q) = \sum_{i,j=1}^2 (b_i - b_0)(b_j - b_0)S_{ij}(Q), \]

where the $b_{i,j}$ are the (complex) scattering lengths of components 1, 2 and the index 0 normally stands for the majority component. In order to separate $S_{11}$, $S_{22}$ and $S_{12}$, the 'contrast', i.e. $(b_i - b_0)(b_j - b_0)^*$ has to be varied. This may be achieved with neutrons by isotopic substitution [see Salva-Ghirladucci, Simon, Guyot & Ansara (1983) for SANS experiments on decomposed Al–Zn–Ag alloys prepared with different Ag isotopes], but the recent progress in the use of continuously tunable X-ray sources (synchrotron radiation) allows one to vary $\Delta b$ within the same sample if the incident wavelength is tuned to the vicinity of an absorption edge and the 'anomalous' scattering is exploited. Such studies have been performed, e.g. for Fe–29 at. % Cr–12.5 at. % Co near the Cr and Fe K edges (at about ten different wavelengths) (Simon & Lyon, 1989). Fig. 9 shows an example for the $S_{CrCr}$, $S_{FeFe}$ and $S_{CoCo}$ partial structure functions calculated from the measurements. In the case of pseudobinary behaviour (corresponding to the two-phase model for sharp interfaces), the dashed lines indicated in the figure are expected. Despite some deviations for $S_{CoCo}$, a test of the condition $S^2_{FeCr} = S_{FeFe}S_{CrCr}$ and further evaluations indicate that the pseudobinary model is appropriate. In the observed ageing range (1.16 to 231 h at 839 K), a coarsening reaction of two well defined phases ($\alpha_1$: Fe–Co rich, $\alpha_2$: Cr rich) is observed, with $Q_m$ proportional to $t^{-0.27}$. The value of the exponent is related to the percolated morphology expected for the two-phase region (Simon & Lyon, 1989).

### 2.4. Beyond the two-phase model

For Cu–42 at. % Ni–15 at. % Fe aged at temperatures between 733 and 823 K, anomalous SAXS experiments have shown deviations from a quasibinary behaviour (Lyon & Simon, 1987, 1988). Although the partial structure functions $S_{ij}$ all look very similar, the peak position, $Q_m$ for $S_{CuCn}$ clearly appears at smaller values than $Q_m$ for $S_{NINi}$ or $S_{FeFe}$ and $S_{FeNi}$ is not equal to $S_{FeFe}S_{NiNi}$ – there are thus two independent structure functions in this system. By analysing the deviations from the closest two-phase model structure function, the authors suggest an Ni/Fe segregation layer around the Ni–Fe-rich core of the precipitating phase, which may arise from differences in the mobility of Ni and Fe. While the Cu distribution is homogeneous in both phases, the Ni/Fe concentration profile thus varies over a larger range. With this assumption, the partial structure
functions can all be understood. A three-phase model (i.e. a second precipitate phase) can be ruled out (Lyon & Simon, 1987). Inhomogeneities in the matrix or the precipitate and segregation at interfaces may of course also occur in binary systems with a well-defined precipitate phase. The simplest case is a concentration gradient of the precipitating species around the newly formed phase during the early stages of growth. This ‘classical’ situation may be easily modelled. A real segregation or ‘trapping’ may occur independently, if this serves to lower the interfacial energy. In a Ti–20 at.% Mo alloy, Fratzl, Langmayr, Vogl & Miekeley (1991) have studied the formation of the coherent \( \omega \) phase below 773 K by SAXS. Although there is scaling (see Fig. 10), the Porod regime is never observed. Instead, a decrease approximately proportional to \( Q^{-3} \) is found. This is modelled by an Mo shell (Mo is expelled upon \( \omega \) formation) surrounding the \( \omega \) particles (see Fig. 11). The growth of the coherent \( \omega \) phase follows \( t^{1/3} \) until the particle radius is about 7.5 nm, but then it slows down considerably. This is interpreted as a progressive hindrance of further growth caused by attractive elastic interactions between particles.

A detailed analysis of the large-\( Q \) behaviour of SAXS measurements on Al–Ag containing Guinier–Preston zones shows that a simple two-phase scattering function is not sufficient to explain the results for ageing above 443 K. A silver coating as schematically shown in Fig. 11 is suggested and yields a satisfactory description of the results (Dubey, 1990; Dubey, Schönfeld & Kostorz, 1991).

### 2.5. Technical alloys

Chemical, electrical, magnetic and mechanical properties of practical alloys are all controlled by the nature, size and distribution of fine-scale inhomogeneities. Often, many components are involved in the formation of the microstructure and many different experimental techniques are necessary to obtain a complete characterization. SAS techniques may frequently help to determine, for example, precipitate sizes and volume fractions. Neutrons are particularly useful as the optimum sample size for SANS is comparable to the real component dimensions. The field has been reviewed not too long ago (Kostorz, 1988b).

A SANS study of a very complex material has recently been reported by Gotoda, Osamura, Furusaka, Arai, Suzuki, Lee, Larbalestier & Monju (1989). From multifilamentary composite wires of less than 1 mm diameter, containing bundles of very thin (16 to 39 \( \mu \)m diameter) filaments of superconducting Nb–Ti, embedded in a normal copper matrix, short pieces were arranged with the axes parallel to each other across the incident neutron beam. The global pinning force density controlling the critical current in the superconducting state depends mainly on the volume fraction of \( \alpha \) precipitates in the \( \beta \) matrix of Nb–Ti. It was possible by SANS to determine changes of the volume fraction of \( \alpha \)-phase particles from 1.3 to 13.4%, depending on the thermomechanical treatment, and to interpret the differences in critical current on this basis, using supporting results from transmission electron microscopy.

### 3. SANS and magnetism

Even if the incident beam is unpolarized, the magnetic neutron–target interaction may be useful in identifying and separating structural and magnetic inhomogeneities in the SAS regime. As polarized neutrons are available at some SANS instruments, a brief summary of the essential features of magnetic SANS may be appropriate.

![Fig. 10. Scaled SAXS for Ti–20 at.% Mo aged at 678 K; \( \bullet \): 2 h; \( \square \): 4 h; \( \bullet \): 8 h; \( \bigcirc \): 16 h; \( \bigcirc \): 32 h. A slope of \(-3\) is indicated. The continuous line is a model function. After Fratzl et al. (1991).](image1)

![Fig. 11. Schematic concentration profiles suggested for ‘coated’ precipitates. Continuous line: Mo concentration (Fratzl et al., 1991) in Ti–20 at.% Mo containing \( \omega \) particles; dashed line: Ag concentration in Al–Ag containing Guinier–Preston zones (Dubey, 1990). The centre of the precipitate is at \( r = 0 \).](image2)
As the neutron has a magnetic moment, it probes, via the magnetic dipole interaction, the local magnetization distribution. Detailed examination (see e.g. Gurevich & Tarasov, 1968) of this interaction shows that of the magnetic scattering amplitude M(Q) related to the Fourier transform of the magnetization density M(r), only the component M^±(Q) perpendicular to the scattering vector Q contributes to any scattering. Just as for the nuclear scattering in the small-angle-scattering region, where the scattering amplitude of the system, F(Q), is obtained by integrating over the locally averaged scattering-length density ρ(r),

\[ F(Q) = \int \rho(r) \exp(iQ \cdot r) \, d^3r, \]  

M(Q) is obtained from the locally averaged magnetization density M(r). If M(r) is given in units of Bohr magnetons per unit volume,

\[ M(Q) = p_0 |M(r)\exp(iQ \cdot r)\, d^3r \]  

with \( p_0 = 2.7 \times 10^{-15} \) m. The magnetic form factor of the individual moments (normally due to unpaired spins) has been omitted as it is close to one in the SANS region. It must be included if the Q range is large, as it decreases more rapidly than the atomic form factor for X-ray scattering.

Moon, Riste & Koehler (1969) have given the four scattering amplitudes for neutron spin-dependent scattering. If the polarization vector of the incident beam is along the z axis and the spin component along the same direction is analysed for the scattered neutrons, the two incident states (++) may remain unchanged (+-) (non-spin-flip, n.s.f.) or 'flipped' (++) (spin flip, s.f.). Nuclear coherent scattering (the nuclear spin-incoherent scattering, though also showing polarization-dependent changes, is not considered here) does not flip the neutron spin and one thus has for the total coherent scattering amplitude

\[ A^{++}(Q) = F(Q) + M^z(Q), \]  
\[ A^{-+}(Q) = F(Q) - M^z(Q), \]  
\[ A^{+-}(Q) = M^z(Q) + iM^x(Q), \]  
\[ A^{-+}(Q) = M^z(Q) - iM^x(Q), \]

One sees immediately that n.s.f. scattering only contains magnetic contributions from effective \( M \) components along z. If Q is parallel to z, \( M_z = 0 \). On the other hand, if s.f. scattering is present, it is exclusively due to effective magnetic components deviating from the polarization axis.

A simple case to consider is magnetic saturation with \( M \parallel H \) (and H along the z axis). Then the scattering is proportional to \( |F(Q) + \pm M(Q)|^2 \) for (+ +) and (− −) scattering if Q is perpendicular to H (no magnetic scattering occurs for Q parallel to H). An unpolarized neutron beam may be taken as composed of 50% positive and 50% negative polarization and the scattering intensity varies as (no polarization analysis)

\[ I(Q) = |F(Q)|^2 + \sin^2 \alpha |M(Q)|^2 \]  

where \( \alpha \) is the angle between Q and H. In particular,

\[ I^{\perp}(Q) = |F(Q)|^2 + |M(Q)|^2 \]  
\[ I^\parallel(Q) = |F(Q)|^2 \]  

where \( \perp \) and \( \parallel \) indicate the directions of Q relative to H.

A number of useful applications of (8)–(10) are possible. In the simple case of a magnetic phase embedded in a non-magnetic matrix or vice versa, the ratio \( I^\perp/I^\parallel \) is independent of the magnitude of Q for complete saturation. Any deviation is an indication of incomplete saturation (then s.f. scattering will occur and an analysis is worthwhile) or for some other scattering contribution. Using measurements of \( I^\perp/I^\parallel \), Beaven, Frisius, Kampmann & Wagner (1986) were able to distinguish scattering contributions from small voids in the presence of somewhat larger Cu precipitates in Fe (the ratio \( I^\perp/I^\parallel \) for voids in ferromagnetic Fe is 1.4, but −11 for Cu precipitates).

In inhomogenous alloys, M(Q) may vary considerably over a wide range of temperatures, as the Curie temperature depends on the chemical composition. Without polarization analysis, magnetic scattering as a function of temperature will give a first indication of the extent and magnitude of magnetized regions. Fig. 12 shows the SANS curves \( I^\perp \) and \( I^\parallel \) for a partially decomposed Ni−14 at.% Al alloy containing small (~5 nm diameter) nonmagnetic Ni₃Al particles in an inhomogeneous matrix, measured at a temperature where the matrix is completely ferromagnetic (194 K). The Al concentration of the matrix is low near the precipitates (~11 at.%) and still high at some distance. The variation of \( I^\perp/I^\parallel \) is

\[ I(10^2 \text{cm}^{-1} \text{s}^{-1}) \]  
\[ Q(\text{nm}^{-1}) \]

Fig. 12. SANS intensities at 194 K, parallel (○) and perpendicular (●) to the magnetic field for inhomogeneous ferromagnetic Ni−Al containing nonmagnetic Ni₃Al precipitates of an average radius of about 2.5 nm.
related to the gradient of saturation magnetization density around the precipitates. As the temperature is increased, those parts containing higher Al concentrations will become paramagnetic first and some additional scattering in the I⁺ part is expected which will initially increase with increasing temperature until, at a higher temperature, the magnetized regions are reduced to shells around the precipitates that finally disappear once T exceeds the highest Tc corresponding to the lowest Al concentration. Preliminary tests using unpolarized neutrons have shown the expected results. As for those parts of the sample where the concentration implies a Tc near the temperature of measurement, the magnetization will fluctuate, measurements with polarized neutrons will be even more instructive.

Measurements of magnetic SANS in zero field for bulk ferromagnets are not advisable if domain walls are present as these will introduce multiple refraction. However, the scattering due to fluctuations of magnetic moments over length scales accessible by SANS may be easily followed for dynamical fluctuations (giant clusters, superparamagnetism, spin-glass behaviour etc.) as a function of temperature. Thus, the formation of fine spin clusters has been revealed by SANS, e.g. in certain Au-Fe alloys in the early experiments of Murani (1976). No sizeable Fe clusters for the spin-glass composition near 15 at.% Fe were observed in a recent SAXS experiment (Yoshida, Langmayr, Fratzl & Vogl, 1989), but the same authors found a short-range-order tendency by Mössbauer spectroscopy and attributed the strong dependence of the magnetic properties on the thermal history in this alloy to temperature-dependent (higher-order) correlations, especially third-neighbour Fe-Fe pairs. More recent SANS experiments have shown magnetic clustering of finite range in Ni-Mn (Moze, Lindley, Rainford & McKPaul, 1985), Pt-10 at.% Fe (Radhakrishna, Gilder, Parette & Menelle, 1989) and in amorphous Fe₉₀Zr₁₀ (Rhyne & Fish, 1985). For a discussion of SANS from disordered magnets in a magnetic field of variable strength, see Cullen & Callen (1986).

A rare example for the use of polarized neutrons in SANS is the study of compositional and magnetic inhomogeneities in the Fe-65 at.% Ni Invar alloy by Komura, Takeda & Endoh (1985) and Takeda, Komura, Miyazaki, Endoh & Itoh (1987). These authors used two different samples, one with natural Ni (scattering length 1.03 x 10⁻¹⁴ m), the other with the isotope ⁶²Ni (-0.87 x 10⁻¹⁴ m), to introduce a change of sign between chemical (nuclear) and magnetic scattering-length densities, ρ(r) and ρ₀M(r) (compared in saturation). If one assumes that the local magnetization is coupled to the Ni-rich regions, the two situations are as indicated in Fig. 13 (schematic, bFe = 0.954 x 10⁻¹⁴ m, i.e. the ρ function has a very small amplitude for natural Ni). If one now looks for n.s.f. scattering, (7a), (7b), in magnetic saturation, I is identical for (+ +) and (− −) and yields the nuclear scattering as before [(10)]. I⁺, however, now contains a cross term

\[ I^{\pm \pm} = |A^{\pm \pm}|^2 = |F|^2 + |M|^2 \pm F(Q)M^*(Q) + c.c. \]  

(11)

Thus, by taking the difference of I⁺⁺⁺ and I⁻⁻⁻, one obtains the interference scattering function between nuclear and magnetic scattering which is controlled by correlations given by

\[ f(\rho(r) - \bar{\rho})(M(r + r') - \bar{M})d^3r'. \]

A change of sign of \( \rho(r) - \bar{\rho} \) will also change the sign of this term. The experiments (after correction for depolarization, calibration etc.) showed a small positive result for \{I⁺⁺⁺ - I⁻⁻⁻\} for the sample prepared with natural Ni. Results for Fe-⁶²Ni at 500 K (i.e. at the Curie temperature) are shown in Fig. 14. The full lines are obtained from a model with paramagnetic Fe-rich regions embedded in a ferromagnetic Ni-rich matrix. However, dynamic spin fluctuations also contribute significantly to SANS in this temperature range (Takeda, Komura, Miyazaki, Endoh & Itoh, 1987).

These experiments with polarized neutrons, performed at a pulsed source (KENS, Tsukuba, Japan), illustrate the possibilities to extract unique information from SANS. Here, and in many other cases, the spin-flip scattering cross sections would give additional insight into the local magnetization. For example, for a concentrated magnetically saturated Co ferrofluid (Pynn, Hayter & Charles, 1983; see also Hayter, 1988), the spin-flip SANS intensity still shows paramagnetic fluctuations.

Finally, long-periodic magnetic structures will give rise to magnetic Bragg peaks in the SANS region. In a cubic FeGe single crystal, very long-range spiral magnetic structures (period 68-70 nm) have recently

![Fig. 13. Schematic of the local compositional changes, ρ(x), and the coupled magnetization changes, M(x), along a direction x in Fe-35 at.% Ni prepared with (a) natural Ni and (b) the isotope ⁶²Ni. After Komura, Takeda & Endoh (1985).](image-url)
been studied by Lebech, Bernhard & Freltoft (1989) on the Risø SANS instrument.

4. Defects in alloys and semiconductors

The role of quenched-in vacancies on phase separation has already been mentioned. Defects in compact materials may also be introduced by plastic deformation and irradiation. Apart from influencing the kinetics of diffusion-controlled phase transformations, new features like clusters of defects or complexes involving solute atoms and defects will introduce additional scattering at small angles. Of course, pores and internal surfaces as they occur, for example, in sintering may also be considered as defects. SAS in this area is covered by Schmidt (1991).

4.1. Irradiation effects in alloys

The characterization of the microstructure of structural materials under irradiation conditions (especially by fast neutrons) is important for existing as well as for future technologies. SAS, in particular with thermal neutrons, has therefore been used, for example, in studies of reactor pressure vessel steels (Solt, Frisius & Waeber, 1989) and of a steel developed for use in the 'Next European Torus' (Albertini, Carsughi, Coppola, Rustichelli, Vlak & Van Dijk, 1991).

The general problem of SAS studies of structural materials is the already inhomogeneous reference state, usually containing decomposition products, carbides, inclusions, which produce a strongly varying SAS signal against which changes, due to irradiation for example, are to be detected. A reasonable evaluation requires some certainty about the stability or the controlled change of this pre-existing microstructure, i.e. information obtained from other experimental methods. New scattering features may be revealed if they occur in the tail region of the reference curve, i.e. if the scattering objects are small. This is frequently the case but the scattering cross sections are also quite small and particular care is necessary to monitor the background (detector 'dark current') during such experiments.

As an example, Fig. 15 shows the SANS cross sections $I^+$ and $I^-$ according to (9), (10) for a reactor pressure vessel steel after irradiation with fast neutrons and a subsequent annealing treatment. The additional nuclear cross section introduced by the irradiation/anneal is extremely small. The ratio $I^+/I^-$ remains independent of $Q$ for all cases, suggesting that there is only one type of defect cluster contributing to the SANS signal. The authors (Solt et al., 1989) suggest that vacancy–copper agglomerates or copper–manganese clusters with a vacancy component are formed during irradiation (Cu and Mn are present in sufficient quantity to account for the required volume fractions). The particle radius in the as-irradiated state increases from about 0.6 nm after a neutron fluence of $3 \times 10^{23}$ neutrons m$^{-2}$ to 0.9 nm at $3 \times 10^{23}$ neutrons m$^{-2}$, with volume fractions up to 0.18%. The anneal seems to increase the Cu

![Fig. 14. Non-spin-flip scattering (macroscopic differential cross sections) from Fe-35 at.% 62Ni, measured for $Q$ perpendicular to the magnetization axis. The sum, $I = (I^+ + I^-)/2$ (full circles, $I > 0$), contains no cross term [cf. equations (11)]. The difference, $I = (I^+ + I^-)/2$ (open circles, $I < 0$), is due to correlations between compositional and magnetic inhomogeneities. The dashed line indicates the incoherent scattering contained in $(I^+ + I^-)/2$, the full lines are the result of a fit of the Guinier approximation with a radius of gyration $R_g = 1.9$ nm. After Takeda, Komura, Miyazaki, Endoh & Itoh (1987).](image)

![Fig. 15. Differential SANS cross section (logarithmic scale) of the defects in a reactor pressure vessel steel after irradiation with about $3 \times 10^{23}$ fast neutrons m$^{-2}$ ($E > 1$ MeV) at 563 K and subsequent anneal (24 h at 693 K). Scattering of an unirradiated reference sample has been subtracted. Measurements were performed in magnetic saturation, parallel (○) and perpendicular (△) to the magnetic field. The solid lines are calculated for spherical particles of average radius $R = 0.83$ nm. $\Delta R/R = 0.246$. After Solt et al. (1989).](image)
content of the clusters. A second irradiation after the anneal introduces a coarsening of the first-generation particles and a new smaller set.

In the work on a modified DIN1.4914 martensitic steel (Albertini et al., 1991), a candidate for use in fusion reactors, defects are produced by irradiation with high-energy He ions. The reference state shows a SANS signal (again measured in magnetic saturation) which is mainly due to large carbides. After irradiation at room temperature (\( E \leq 38 \text{ MeV} \), 500 implanted He ions in \( 10^6 \) target atoms) and an anneal for 2 h at 1073 K, He bubbles are known to form [determined by transmission electron microscopy (Caciuffo, Coppola, Rustichelli & Ray, 1988)]. There is a small but noticeable additional SANS intensity due to the He bubbles. The authors (Albertini et al., 1991) even arrive at a size distribution centred around a radius of 1 nm.

4.2. Defects in semiconductors

In bulk semiconductors, very sensitive SAS studies of defects are possible because these materials are usually very pure and homogeneous. Thus, the precipitation of trace impurities (10-40 in \( 10^6 \)) of oxygen in Czochralski-grown Si single crystals in the form of amorphous SiO\(_2\) leads to a very clear anisotropic SANS pattern of cross-like shape for the incident beam parallel to \( (100) \) after high-temperature anneals as typically employed in semiconductor device fabrication. Takeda, Komura, Ohsawa & Honda (1987) and Messoloras, Schneider, Stewart & Zulehner (1988, 1989) have attributed this scattering to precipitate platelets a few nanometres thick lying on \{100\} planes with the long edges (several tens of nanometres) along \( (100) \). The volume fractions are not much larger than \( 10^{-6} \).

Hydrogenated amorphous silicon (a-Si:H) is a promising material for solar cells. In nondevice-quality a-Si:H, microvoids have been clearly revealed by different techniques (Mahan, Williamson, Nelson & Crandall, 1989; Elliot, 1989), including SAS. From their work on glow-discharge-deposited device-quality a-Si:H, combining SAS and infrared measurements, Mahan et al. (1989) conclude that microvoids of an average radius of about 0.5 nm are present and that each of them contains at most four–nine bonded H atoms. This is not sufficient to reduce the number of dangling bonds to the levels observed and some reconstruction is therefore postulated.

Fratzl, Klaumünzer, Rammensee & Vogl (1990) have introduced additional defects into glow-discharge-deposited a-Si:He by irradiating samples 30 \( \mu \)m thick with 360 MeV Xe ions from a heavy-ion accelerator. The damage distribution was homogeneous within the samples. After warm up to room temperature, SAXS measurements were performed using a linear position-sensitive detector. Rotating this detector around the incident-beam direction showed no anisotropy of the scattering pattern, confirming that the damage zones fully overlapped. Fig. 16 shows the results. The scattering observed for the unirradiated sample [in a \( Q \) range extending to smaller values than evaluated by Mahan et al. (1989)] seems to be largely unaffected by the irradiation which makes it unlikely (Fratzl et al., 1990) that this scattering effect is due to voids (as they should be modified by the irradiation). The irradiation-induced defect clusters lead to a large SAS peak which appears at smaller \( Q \) values for higher fluences. An evaluation on the basis of the two-phase model and an approximation for late-stage scaling (Fratzl & Lebowitz, 1989) leads to average void radii from 1.6 to 2.3 nm and volume fractions from about 5 to 13% (which compares favourably with macroscopic density changes). The interference peak indicates a preferred distance between the voids (7 to 8.5 nm) which may be related to the average size of the active damage zone. From SAXS experiments alone, it is not possible to decide whether the voids contain any hydrogen.

5. Concluding remarks

This survey is limited to only a few areas of small-angle scattering in materials science and only bulk phenomena in the single-scattering limit have been considered. Many interesting studies at small angles are possible also for two-dimensional systems. Apart from reflectivity and refraction, true small-angle scattering at grazing incidence (i.e. scattering due to the

![Fig. 16. SAXS results for Xe-irradiated a-Si:H (logarithmic scales). The broken line is a \( Q^{-3} \) fit to the scattering data (*) of the unirradiated sample. Fluences (in \( 10^{17} \text{ Xe m}^{-2} \)): □: 1; ◦: 1.9; □: 3.1; ◦: 4.4; ▽: 4.5. After Fratzl et al. (1990).](image-url)
refracted beam, perpendicular to the plane defined by incident and refracted beam) has recently been introduced (Levine, Cohen, Chung & Georgopoulos, 1989) as a very sensitive method for the study of scattering objects on surfaces or at interfaces.

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