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ANTI-PHASE DOMAINS. A NOTE ABOUT X-RAY DIFFRACTION LINE PROFILES IN THE TANGENT PLANE APPROXIMATION

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ABSTRACT

The expected X-Ray Diffraction peak profile for two domain distributions which often have been assumed to hold in anti-phase domain theory is given. It is shown that in both cases the expected line profile must be Cauchy-like. In spite that the assumption of one or another distribution may lead to a difference in the measured mean domain thickness by a factor of 1.5, the form factor of both curves is similar enough so as to make extremely improbably that this distributions could be differentiate from the experimental profile analysis results alone.

RESUMEN

Se muestran los perfiles teóricos de los picos de difracción obtenidos para dos distribuciones que a menudo han sido tomadas como base en la teoría de los dominios anti-fase. En ambos casos el perfil esperado debe ser del tipo Cauchy. A pesar de que en dependencia de la distribución asumida se pueden obtener diferencias en el tamaño promedio de los dominios en un factor hasta del orden de 1.5, el factor de forma de ambas curvas es lo suficientemente similar como para hacer extremadamente improbable que estas distribuciones puedan ser diferenciadas a partir del análisis del perfil experimental de los picos de difracción solamente.

Line shape analysis is a common procedure in the determination of stress, small crystal size and mean domain size in diffractometry. In the case where the unknown is the mean domain thickness in materials showing substitutional disorder, the obtention of the domain thickness distribution from the experimental data is a problem which has not been

reasonably solved yet. This fact introduces an indetermination in the measured mean domain thickness, which obviously depends of the particular domain size distribution occurring in the crystals. In some cases, a certain domain distribution has been a priori assumed to hold: the mean domain thickness is obtained adjusting the experimental data to this particular distribution /1,2,3,4/. In others, the method proposed is approximate and complex enough so as to make some results doubtful /5,6,7/, or it keeps some of the a priori assumptions, as it is to suppose that the domain distribution q(M), where M is proportional to domain thickness, is such that q(M)=1/D as M tends to zero /7/, being D the mean domain thickness.

In a previous paper /8/, based in a discrete approach to the problem /9,10/, the expressions for the variance and the integral breadth of reflections as a function of mean domain thickness were derived for two different domain size distributions: that of domain growth with occasional "mistakes" or defects,

$$q(M)dM = \Lambda \exp(-\Lambda M)dM \qquad (1.1)$$

and the Lifschitz's multiple nucleation and growth model (see /11/),

$$q(M)dM = \gamma^2 M \exp(-\gamma M)dM \qquad (\gamma = 2\Lambda) \qquad (1.2)$$

M is the distance in units of $[\bar{a}_1']$, the cell length along the [hkl] direction under consideration, $\Lambda = |\bar{a}_1'|/D$, and q(M)dM the probability that the length (or thickness) of a particular domain be inside the limits (M, M+dM). In the following, the line profile expressions obtained from these two distributions are shown and discussed. It is worth to notice that even distribution (1.1) has been most used in the analysis of anti-phase domain diffraction theory, mainly because of its simple mathematical expression, its physical sense at M=0, where $q(M) = \Lambda$, is not clear at all. For distribution (1.2) q(M) tends to zero as M does, as it must be.

LINE PROFILE EXPRESSIONS

In the case of substitutional disorder, the intensity of a superlattice reflection in the tangent plane approximation /12,13/ may be expressed as

$$I(s) = J(0) + 2\sum_{m=1}^{\infty} J(m)\cos(2\pi ms), \qquad (2.1)$$

where J(m) is the mean value of the structure factor product $F_{j_1j_2j_3}F^*_{j_1'j_2j_3}$ throughout the crystal for a given m, being $m = j_1' - j_1$ and $s = |\bar{a}_1'|(2\sin\theta/\lambda - n/d)$; here θ is the Bragg's angle, λ the x-ray wavelength, n the order of

reflection and d the real interplanar distance /8,9/. If it is assumed that:

i) domain walls may be formed between any two types of domain, and

ii) the N allowed domain types show up in the crystal with the same probability,

it is obtained, for the probability distributions (1.1) and (1.2), respectively (see /8/):

$$J(m) = J(0)\exp\{-\Lambda(N/(N-1))m\} \qquad (2.2)$$

$$J(m) = J(0)\left\{\cos(\gamma m/\sqrt{N-1}) + ((N-2)/2\sqrt{N-1})\sin(\gamma m/\sqrt{N-1})\right\}\exp(-\gamma m) \qquad (2.3)$$

The substitution of these expressions in (2.1) leads, after some work, to the desired peak profile expressions for these two particular distributions, which are shown in table I. The expressions are normalized in J(0), which is proportional to the integrated intensity. Both curves are symmetric, with its maximum intensity at s=0 (Bragg's condition for diffraction maxima).

Table I

$$I(s) = \frac{e^{Q} + e^{-Q}}{e^{Q} + e^{-Q} - 2\cos\beta} \qquad (2.4)$$

$$I(s)\ \frac{e^{2\gamma}-e^{-2\gamma}-2\{\cos\alpha(e^{\gamma}-e^{-\gamma})-\delta\sin\alpha(e^{\gamma}+e^{-\gamma})\}\cos\wp-4\delta\sin\alpha\cos\alpha}{[e^{\gamma}+e^{-\gamma}-2\cos\alpha\cos\wp]^2-4\sin^2\alpha\sin^2\wp} \tag{2.5}$$

$Q=\Lambda\ (N/(N-1));\ \gamma=2\Lambda\ ;\ \alpha=\gamma/\sqrt{N-1}\ ;\ \delta=(N-2)/2\sqrt{N-1}\ ;\ \wp=2\pi s$

DISCUSSION AND CONCLUSIONS

To evaluate and characterize this complex expressions, it was found necessary to calculate by computer the form factor -or Langford's factor- 2w/B/14/, where 2w is the peak half-width and B the integral breadth, for different mean domain thickness with N=4 and 8, as corresponds, for example, to the presence of antiphase domains in Cu_3Au and $LiFe_5O_8$, respectively /1,7/, with the following results.

Distribution (1.1). In both cases, N=4 and N=8, the dependence of the form factor with Λ is similar, scantily noticeably. This factor changes from a value of 0.635 in the case of relatively large domains (Λ=0.01) to a value of 0.645 in the case of very small domains (Λ=0.25), being the profiles esentially Cauchy-like.(For a Cauchy--Lorentz profile, 2w/B = 0.637).

Distribution (1.2). In the limit for small domains the form factor takes values near 0.65 in both cases, N = 4 and 8. When larger domains are considered, the departure

from the Cauchy profile is somewhat more pronounced in the case N=4 than for N=8. For Λ=0.05 and N=4, 2w/B=0.725, while for N=8 the form factor is 0.683.

This results shows that in both cases, distributions (1.1) and (1.2), the expected line profiles must be very similar and Cauchy-like, and only in the case of large domains (small broadening of the superlattice lines) should be expected some departure of this behaviour, and not too marked. (For example, the form factor for a Gaussian profile is 0.9395). The departure should be more noticeably in the case of N=4, if noticed at all, because for small broadening the "window" or instrumental function folding the physically broadened profile has a considerably weight in the results of the unfolding procedure and the precision of measurement. It is concluded that for this two different domain length distributions we must expect a similar, hardly differentiable, x-ray line profile, with independence of the degree of broadening of the peaks. This fact points out that very different domain distributions, not necessarily (1.1) or (1.2), with different mean domain thickness, may provide very similar x-ray line profiles. In the inverse case, given a Cauchy-like x-ray diffraction line profile, and even in the absence of broadening caused by small crystal size or stresses, and with independence of the particular method used to unfold the peaks, it seems extremely improbable that the domain distribution occurring in the crystals could be reasonably approximated to (1.1) or (1.2), even with the help of the variance, as it has been suggested /8/, because of the experimental errors and the inaccuracy asociated to the unfolding procedure. This behaviour introduces an indetermination in the measurement which can not be removed, because the mean domain thickness may differ, in the case of distributions (1.1) and (1.2), up to a factor of 1.5, in dependence of which distribution is assumed to hold /15/. For an experimental non Cauchy-like profile there is no basis for assuming neither distribution. This fact usually has not been taken into account, leading to questionable results.

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