

$(v/c) \ll 1$ and $(v_n/c)^2 \ll 1$ can be assumed, $\Delta_1/(\hbar\omega)$ and $\Delta_2/(\hbar\omega)$ are much smaller than unity. With the use of the power series for the terms in square brackets in (B1), we have

$$X_2^* \mathbf{B}^+ X_1 = X_2^* X_1 (\hbar\omega)^{-1} [1 + (\Delta_1/\hbar\omega) + (\Delta_1/\hbar\omega)^2 + \dots], \quad (B3a)$$

$$X_1 \mathbf{B}^- X_2^* = X_1 X_2^* (\hbar\omega)^{-1} [-1 + (\Delta_2/\hbar\omega) - (\Delta_2/\hbar\omega)^2 + \dots]. \quad (B3b)$$

From these, it follows that

$$\langle \varphi_a | X_2^* \mathbf{B}^+ X_1 + X_1 \mathbf{B}^- X_2^* | \varphi_a \rangle = \langle \varphi_a | X_1 X_2^* | \varphi_a \rangle (mc^2)^{-1} [1 + (v/c)^2 + \dots], \quad (B4)$$

where odd terms of p are dropped.

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Structure Factors and Debye Temperatures of Al–Li Solid-Solution Alloys

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Abstract

By combining the accurate low-angle X-ray structure factors of Al–Li solid-solution alloys (containing 5.25 and 8.06 at.% Li) determined by the critical voltage technique in high-energy electron diffraction (HEED) with higher-angle values obtained by interpolation between best pure-element form factors, a complete set of accurate X-ray structure factors for these alloys has been produced. From the measured Debye–Waller factors for the alloys it was found to be difficult to determine a Debye temperature trend with composition for Al–Li solid-solution alloys because of the extent of the experimental errors, although the results suggest that the Debye temperatures of the alloys are higher than that of pure aluminium. This is obviously consistent with an increase in Young's modulus; *i.e.* the stiffness of the alloys appears to be greater than that of pure aluminium. This increase appears to arise predominantly from an increase in the force constant between nearest-neighbour (n.n.) lithium atoms in the alloy as compared with the value for pure lithium. This occurs because n.n. lithium atoms are closer together in Al–Li solid-solution alloys than they are

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in pure lithium. Because the lithium atoms are closer together in the alloys, the electron charge density, ρ , associated with the valence electrons in the alloys is likely to be higher than if ρ is considered unchanged by alloying. This suggested increase in the charge density of the alloy valence electrons was confirmed, as the experimental 111 low-angle structure factors of the alloys were found to be significantly higher than the equivalent values obtained by interpolation between the best pure-element form factors. Such electronic changes are to be expected for Al–Li alloys as aluminium and lithium have a valency difference of two.

1. Introduction

When a crystal is set at a Bragg reflecting position in electron diffraction, the intensity of the diffracted beam is usually strong owing to the constructive interference of waves scattered in the diffracted-beam direction. However, for reflections higher than first order in a systematic row, at a particular electron accelerating voltage known as the critical voltage, V_c ,

the diffracted-beam intensity can be very small owing to destructive rather than constructive interference. [See, for example, Lally, Humphreys, Metherell & Fisher (1972).] The critical voltage is very sensitive to the low-order Fourier coefficients of the crystal potential for the systematic row concerned, and hence can be used to determine these and related quantities with high accuracy. In particular, low-angle X-ray structure factors can be measured with an accuracy which far exceeds conventional X-ray methods.

Recent structure-factor determinations of cubic elements and primary binary cubic solid solutions have been accurate enough for electron charge redistributions due to alloying and Debye temperature trends with alloy composition to be determined (Smart & Humphreys, 1978, 1980; Fox, 1984; Fox & Fisher, 1986). This high accuracy has been achieved by measuring the low-angle X-ray structure factors by the critical voltage method in HEED and obtaining higher-angle values from the best pure-element form factors. In addition, this high accuracy has allowed the measurement of the temperature-independent atomic mean-square displacements (m.s.d.) arising from the atomic radius difference between the two types of atom comprising the alloy, and, where this difference is significant, the extent of short-range order can be determined by these accurate structure-factor measurements (Shirley & Fisher, 1979; Kuroda, Tomokiyō & Eguchi, 1981; Fox, 1984; Fox & Fisher, 1986).

There are many binary cubic alloy systems for which useful fundamental information can be obtained from these sorts of experiments (Fox & Fisher, 1986), and the object of the present work is to produce accurate sets of structure factors for two Al-Li solid-solution alloys and from these deduce their Debye temperatures and any possible electron charge redistribution due to alloying. These measurements should give a fundamental insight into some of the important properties of these alloys (apart from their low density) which make them an attractive proposition for aerospace applications.

2. Theory

Theories for the structure factors of binary cubic alloys have been developed by Shirley & Fisher (1979), Fox (1983), Fox & Shirley (1983), Fox (1984) and Fox & Fisher (1986). In solid solutions, composition, temperature and short-range order affect the structure factor only through the average atomic scattering factor f , which is given by

$$f = m_A f_A \exp(-B_A \sin^2 \psi / \lambda^2) + m_B f_B \exp(-B_B \sin^2 \psi / \lambda^2). \quad (1)$$

In this expression ψ is the Bragg angle and λ the electron (or X-ray) wavelength. The atom fraction of

A (or B) atoms is m_A (or m_B) and the respective Debye-Waller factors are B_A (or B_B). The atomic scattering factors (form factors) in the alloy are f_A and f_B .

The form factors f_A and f_B in the alloy are, in theory, functions of composition and short-range order. However, alloying only causes electron charge redistribution among the valence electrons, which means that only the low-angle values of f_A and f_B will be significantly modified by alloying (Fox & Fisher, 1986). Higher-angle form factors are constant and equal to the pure-element form factors (corrected for lattice-parameter changes).

For binary cubic alloys with a small atomic radius difference such as Al-Li (radius mismatch $<1.0\%$), the Debye-Waller factors B_A and B_B are equal (Shirley, Thomas, Lally & Fisher, 1975) so that $B_A = B_B = B$ and contributions to B come only from thermal vibrations. In the harmonic approximation, the usual quantum expression for B is

$$B = \frac{6h^2}{KA} \left(\frac{T\varphi(\theta/T)}{\mu\theta^2} + \frac{1}{4\mu\theta} \right), \quad (2)$$

where h is Planck's constant, K is Boltzmann's constant, A is the atomic mass unit, φ is Debye's function, T the absolute temperature, θ the Debye temperature and $\mu = m_A \mu_A + m_B \mu_B$ where $\mu_{A(B)}$ is the atomic weight of an A(B) atom.

Using a nearest-neighbour (n.n.) central force model and the harmonic approximation Shirley (1975) derived an expression for the Debye temperature θ of the alloy, expressing this in terms of θ_A and θ_B , the Debye temperatures of the pure elements comprising the alloy, thus:

$$\mu\theta^2 = m_A \mu_A \theta_A^2 + m_B \mu_B \theta_B^2 + (1 - \alpha_1) \times (\tau - 1) m_A m_B (\mu_A \theta_A^2 + \mu_B \theta_B^2) \quad (3)$$

where α_1 is the n.n. Cowley Warren short-range order parameter; and τ is a constant given by

$$\tau = 2k_{AB} / (k_{AA} + k_{BB}) \quad (4)$$

where $k_{AA(BB)}$ is the force constant between nearest-neighbour A-A (B-B) atoms and k_{AB} is the n.n. force constant between an A-B atom pair. Equation (3) depends on the average force constants between different atom pairs being unchanged by composition. For solid-solution alloys comprising two elements with different valencies and/or with a large atomic radius difference there will almost certainly be force-constant changes associated with alloying; such force-constant changes have been detected in CuAu by Fox (1984). Care must therefore be taken when interpreting the results obtained from the application of (3) to Debye-temperature determinations of binary cubic solid solutions which fall into these categories. In addition, (3) depends on the elements and the solid-solution alloy being isostructural. Al-Li solid

solutions are f.c.c., but pure Li is b.c.c., and so if B atoms refer to lithium, then θ_B represents a hypothetical Debye temperature for 'f.c.c. lithium' with a slightly smaller lattice parameter than aluminium.

From (1) (with $B_A = B_B$) and (2) it is clear that to measure Debye temperatures in Al-Li alloys and to detect changes in low-angle structure factors due to electron charge redistribution, accurate room- and low-temperature measurements of these must be made for at least two alloy compositions. This can be done by making critical voltage measurements in the lowest-order systematic rows of the alloys in the cold stage of the high-voltage electron microscope (HVEM). Values for the higher-angle structure factors of the alloys can be obtained by interpolation between best pure-element form factors (Fox, 1984).

3. Experimental

As outlined in §1, a second- or higher-order Bragg-excited reflection in a systematic row can minimize at a critical voltage as a result of the destructive interference of the electron waves. These minimizations can be detected in conventional Kikuchi-line (K -line) and convergent-beam electron diffraction patterns very easily as the dark/bright K -line pair associated with the straight-through and Bragg-diffracted beams disappear at V_c . Furthermore, the central maximum of the rocking-curve profile in the Bragg-excited convergent-beam disc goes through a pronounced minimum at V_c , which combined with the Kikuchi-line information can give a very accurate (± 1 kV) critical voltage value (Sellar, Imeson & Humphreys 1980). Alternatively the central maximum of the dark-field bend contour associated with the Bragg-diffracted beam can be monitored, and this will also pass through a minimum at V_c (Lally *et al.*, 1972). In addition to the K -line behaviour described previously, other characteristic changes in the K -line diffraction pattern can help to determine V_c accurately; for example, for a second-order minimization the 000 bright/dark K -line pair show an abrupt symmetry reversal on passing through V_c (Lally *et al.*, 1972). This information can also help to improve the accuracy of the determination of the critical voltage. A critical voltage value can be analysed simply using n -beam dynamical theory to give a value for the first-order structure factor (for electrons) of the systematic row concerned. This can be converted to the first-order X-ray structure factor by the use of the usual formula (Ibers, 1958).

The 111, 200 and 220 systematic rows of Al and two Al-Li solid-solution alloys were theoretically examined for potential critical voltages using a suitable computer program [see, for example, Fisher (1968)]. Only two suitable critical voltages below 3 MeV (the highest voltage available on any HVEM)

were found; these minimizations were associated with the 222 and 400 reflections. In this analysis the free-atom relativistic Hartree-Fock (RHF) form factors of Doyle & Turner (1968) were used. The Debye-Waller factors for the alloys were calculated from (2) and (3) with $\alpha_1 = 0$, $\tau = 1$ and with $\theta_{Al} = 395$ K (Dingle & Medlin, 1972) and $\theta_{Li} = 384$ K [a value calculated from the m.s.d. quoted by Lonsdale (1968) as coming from the measurements of Pankow (1936) for the pure element]. These results are shown in Table 1 along with the experimental measurements.

Two samples of Al-Li solid-solution alloys containing 5.25 and 8.06 at.% lithium were supplied by the Aluminium Company of America. These were cold-rolled into a sheet 0.25 mm thick from which discs of 3 mm diameter were punched. These discs were solution-treated for 30 min in pure argon at a pressure of 1 bar (1 bar = 100 kPa) and temperature of 813 K, and then quenched rapidly into water. This procedure ensured that there were minimal losses of volatile lithium during heat treatment, and that the samples were single-phase solid solutions. Some of the solution-treated discs of the Al-8.06 at.% Li alloy were given an age-hardening treatment of 473 K for 12 h so that about 5% of the solid solution transformed into Al_3Li δ' precipitates of about 40 nm in size. Thin samples for transmission electron microscopy were prepared by jet electropolishing using a solution of 3% perchloric acid, 35% *n*-butoxyethanol and 62% ethanol at 40 V and < 248 K.

The 222 and 400 critical voltages (V_c^{222} and V_c^{400}) in both alloys were measured using the convergent-beam technique (Tomokiyo, Kuroda, Matsuhata & Eguchi, 1980; Sellar *et al.*, 1980) at room temperature (293 K) and at 92 K in a Kratos 1.5 MeV HVEM. These results are shown in Table 1 together with the V_c^{222} and V_c^{400} values for pure aluminium measured by other workers and the theoretical predictions.

The minimum probe size obtainable on the Kratos 1.5 MeV HVEM for the routine generation of convergent-beam patterns is around 120 nm at 1500 kV and this increases at lower voltages. To obtain improved convergent-beam patterns, the more complex non-routine procedure of Sellar *et al.* (1980) could be adopted to generate probe crossovers of ~100 nm at 400 kV improving to 40 nm at 1 MeV. This method can allow critical voltages to be measured to within ± 1 kV. In the present work the best accuracy obtainable was ± 10 kV.

The errors in the measurement of the temperature are difficult to assess. The actual error on the HVEM cold-stage digital readout is ± 1 K, but the specimen may be somewhat higher in temperature because of poor thermal contact between the stage and the sample and the possibility of heating by the electron beam (Fox & Fisher, 1986). However, before low-temperature measurements were commenced, the sample was allowed to 'settle' for about half an hour

Table 1. Debye temperature θ , Debye-Waller factors B and critical-voltage measurements V_c , in Al and quenched Al-Li solid-solution alloys

| θ (K) | B (\AA^2) | At.% Li | Temperature (K) | V_c^{222} (kV) | | V_c^{400} (kV) | |
|--------------|--------------------------|---------|-----------------|------------------|------------|------------------|------------|
| | | | | Theory | Experiment | Theory | Experiment |
| 395 (1)† | 0.849 (5)† | 0.00 | 295 | 472 | 425* | 987 | 918 (5)* |
| 399.5 (100) | { 0.855 (50) 0.37 (5) | 5.25 | 293 | 493 | 465 (10) | 1022 | 975 (15) |
| | | 5.25 | 92 | — | 535 (10) | — | 1110 (15) |
| 397 (10) | { 0.902 (50) 0.39 (5) | 8.06 | 293 | 504 | 475 (10) | 1041 | 990 (10) |
| | | 8.06 | 92 | — | 550 (10) | — | 1140 (15) |

* Source of pure Al V_c data is Thomas, Shirley, Lally & Fisher (1974).† Source of pure Al θ and B data is Dingle & Medlin (1972).

with the beam off once the thermocouple showed 92 K, and the beam interaction time with the specimen during critical-voltage measurements was kept to a minimum. This procedure ensured that the sample was thoroughly cooled throughout and as close as possible in temperature to the values indicated by the cold-stage readout.

The experimental results shown in Table 1 were used to determine the experimental 111 and 200 structure factors and Debye-Waller factors shown in Tables 1, 2 and 3. This analysis is outlined in the next section.

4. Analysis of data

In order to analyse the data of Table 1 and to produce a complete set of X-ray structure factors for the two alloys under consideration, it is necessary to have accurate values of the higher-angle alloy structure factors. Complete sets of these (up to $hkl = 420$) were obtained by curve fitting to accurate pure-element form factors of Al and Li and then interpolating. For Al, Fox (1985) and Fox & Fisher (1986) have shown that the X-ray measured form factors of Inkinen, Pesonen & Paakkari (1970) give excellent agreement (within 1 kV) with those obtained from the pure-element critical-voltage measurements shown in Table 1, and these were therefore adopted in the calculations. For Li, no accurate measured or band-structure-calculated form factors are apparently available and so only the free-atom tabulated values can be used; the best of these appear to be the RHF values of Doyle & Turner (1968). The use of these RHF form factors for Li in this calculation only introduces very small errors into the structure factors of the Al-Li solid solutions based on best pure-element form factors, even at the lowest angles. Calculations show that even if the Li form factors are 10% inaccurate the error introduced into the 111 structure factor of an Al-8.06 at.% Li solid solution is less than 0.25% and lower for higher angles. Fox (1986) has noted that Doyle & Turner (1968) form factors are at most 5% different from the actual values for solid elements, even for very light atoms such as Be ($Z = 4$). This suggests that the error introduced into the structure factors of Al-Li solid solutions calcu-

lated from the best pure-element values described above is at most 0.13%, and can therefore be safely ignored. The structure factors deduced from these best pure-element form factors for the two alloys are shown in Tables 2 and 3, together with the RHF free-atom and experimental values.

The critical-voltage measurements in the two Al-Li alloys shown in Table 1 were then analysed in the usual way [see, for example, Lally *et al.* (1972), Shirley *et al.* (1975), Shirley & Fisher (1979), Fox & Fisher (1986)] to produce Debye-Waller factors, Debye temperatures and the 111 and 200 low-angle X-ray structure factors. These results are shown in Tables 1-3. The errors in these measurements were calculated in the manner described by Lally *et al.* (1972), Sellar *et al.* (1980) and Fox (1984). From the Debye-Waller factor and Debye temperature results, values of $\tau = 1.15$ (36) and $\theta_{Li} = 450$ (100) K for the effective Debye temperature of 'f.c.c. Li' in the alloys were calculated. The error in θ_{Al} (± 1 K) obtained from the results of Dingle & Medlin (1972) seems rather small; the authors consider that an error of ± 3 K is more likely, and this value was therefore adopted in the error calculations for τ and θ_{Li} . As the atomic-radius difference is very small, static contributions to the Debye-Waller factor B and the effects of short-range order are negligible (Fox & Fisher, 1986) and were therefore ignored.

5. Discussion

5.1. Structure-factor values

The electron charge distribution of pure aluminium has been investigated by Smart & Humphreys (1980), and it appears that as a result of bringing aluminium atoms together in solid Al the free-atom RHF spherical electron charge distribution is changed in such a way that there is a depletion of electrons from the atomic regions with a redistribution between the atoms such that there is a depletion of electrons from the tetrahedral interstitial sites. As aluminium is trivalent its Fermi surface is very complex (Cracknell, 1971) and it is not easy to correlate the shape and volume of this with the electron charge distribution presented by Smart & Humphreys (1980). To the

Table 2. Room-temperature X-ray structure-factor (F_{hkl}) values for Al-5.25 at.% Li

| hkl | $\sin \theta/\lambda$ (\AA^{-1}) | F_{hkl} (RHF free atom) | F_{hkl} (pure element) | F_{hkl} (experimental) |
|-------|--|------------------------------|-----------------------------|-----------------------------|
| 111 | 0.21394 | 32.939 | 32.415 | 32.645 (110) |
| 200 | 0.24704 | 30.82 | 30.542 | 30.55 (15) |
| 220 | 0.34936 | 25.364 | 25.125 | |
| 311 | 0.40966 | 22.301 | 21.995 | |
| 222 | 0.42788 | 21.348 | 21.052 | |
| 400 | 0.49407 | 17.868 | 17.797 | |
| 331 | 0.53840 | 15.657 | 15.766 | |
| 420 | 0.55239 | 14.999 | 15.149 | |

Table 3. Room-temperature X-ray structure-factor (F_{hkl}) values for Al-8.06 at.% Li

| hkl | $\sin \theta/\lambda$ (\AA^{-1}) | F_{hkl} (RHF free atom) | F_{hkl} (pure element) | F_{hkl} (experimental) |
|-------|--|------------------------------|-----------------------------|-----------------------------|
| 111 | 0.21399 | 32.083 | 31.578 | 33.135 (110) |
| 200 | 0.24709 | 30.001 | 29.733 | 29.72 (15) |
| 220 | 0.34944 | 24.618 | 24.389 | |
| 311 | 0.40975 | 21.593 | 21.301 | |
| 222 | 0.42797 | 20.653 | 20.371 | |
| 400 | 0.49418 | 17.231 | 17.166 | |
| 331 | 0.53852 | 15.065 | 15.144 | |
| 420 | 0.55251 | 14.421 | 14.560 | |

authors' knowledge no Fermi surface measurements have been made on Al-Li solid-solution alloys. In addition, it is not possible to produce electron charge density maps for Al-Li solid solutions from the structure factors presented in Tables 2 and 3 as the lithium atoms are distributed at random in the alloy.

However, it is very easy to interpret the structure-factor results of Tables 2 and 3. It is clear from these that the 111 X-ray structure factor, F_{111} , is significantly increased by alloying, whereas F_{200} appears to remain unaffected. This suggests that the structure factors having $(hkl) > (200)$ are also unaltered by alloying as they occur at higher angles. The increase in F_{111} can be explained by the following argument. In pure lithium the n.n. distance is 3.031 Å whereas the n.n. distance in Al-Li solid-solution alloys is about 2.86 Å. This means that the valence electrons in the alloy are contained in a much smaller volume than if they were in the pure elements. Consequently, the valence electron density of the Al-Li solid solutions will be higher than equivalent alloys in which the lithium atoms had suffered no reduction in nearest-neighbour distance. This is reflected in the experimental values of F_{111} which are much higher than those obtained by interpolation between the best pure-element form factors for both the alloys studied.

5.2. Debye temperatures

As a result of alloying lithium with aluminium, Table 1 suggests that the Debye temperature is increased, although the errors are rather large to be conclusive about this. However, if this is the case, the average force constant per unit mass, and therefore Young's modulus, E , will be increased, and it is well known that making lithium-alloying additions to aluminium causes an increase in E and gives the desirable combination of an increase in stiffness and a reduction in density. It would seem that this increase in stiffness comes about because the force constant between n.n. lithium atoms in the alloy (k_{BB}) is higher than its value in the pure element. Since $\theta_{Li} = 378$ (16) K (pure element) (Pankow, 1936) and $\theta_{Li} = 450$ (100) K (alloy), and the n.n. force constant is proportional to the square of the Debye temperature (in the classical regime), then k_{BB} in the alloy is

1.42 (45) times its values in pure lithium. As mentioned previously, the contributions to the Debye-Waller factors B from both atomic-radius mismatch and short-range order are very small and can be ignored.

5.3. Effect of age hardening

222 and 400 critical-voltage measurements were also made on the Al-8.06 at.% Li two-phase alloy which had been age hardened at 473 K for 12 h. No changes in V_c^{222} or V_c^{400} within experimental error were detected. Calculations based on the δ' -Al₃Li precipitates and an Al-25 at.% Li solid solution having the same Debye temperature predict no change in V_c^{222} and an increase of about 3 kV for a V_c^{400} measurement on the $\alpha + \delta'$ two-phase 8.06 at.% Li alloy; this small change in V_c^{400} is obviously undetectable within the accuracy of the present work. Unfortunately the precipitates of δ' were too small (~40 nm) for the critical voltages of δ' -Al₃Li to be measured independently of the solid solution, so that the effects of ordering could not be studied.

6. Concluding remarks

(1) The small changes in low-angle X-ray structure factors which arise due to alloying in a primary binary solid solution can be detected by the critical-voltage method in HEED, and this has been demonstrated for two Al-Li alloys.

(2) The 111 low-angle X-ray structure factor in Al-Li solid-solution alloys is higher than F_{111} values obtained by interpolation between best pure-element form factors. This means that alloying causes an increase in the valence electron charge density. This increase arises because the n.n. distance in the Al-Li solid-solution alloys is about 6% less than in pure lithium.

(3) Because of the closer proximity of n.n. lithium atoms in the alloys, the n.n. force constant between Li atoms is 1.42 (45) times its value in the pure element. This suggests that the Debye temperatures and consequently the Young's modulus of Al-Li solid solutions are higher than in pure aluminium.

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Anisotropy in the Variation of Serially-Measured Integrated Intensities

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Abstract

The variation (often decline) in intensity standards measured during a typical X-ray diffraction structure determination is commonly corrected by means of an isotropic polynomial expression of the form $I_t = I_0(1 - \sum_n A_n t^n)$, where t is the exposure time in hours, I_0 is the integrated intensity at zero exposure and $1 \leq n \leq 7$. A linear decline corresponding to $n = 1$ is reported in many studies. In the simplest (linear) anisotropic case, the variation may be represented by

$$I_t = I_0[1 - t(\alpha_{11}h^2 + \alpha_{22}k^2 + \alpha_{33}l^2 + 2\alpha_{12}hk + 2\alpha_{13}hl + 2\alpha_{23}kl)/(h^2 + k^2 + l^2)]$$

where the α_{ij} are coefficients of a radiation-damage-effect ellipsoid. Higher-order and exponential time dependences have also been investigated. The results of applying the anisotropy relation both to an organometallic and an inorganic structure, as evalu-

ated by the method of least squares, are presented. For each case the linear anisotropic correction leads to significant reductions in R_{int} and wR_{int} , with additional improvement resulting from inclusion of quadratic decline correction terms. The smallest number of experimental data required to evaluate the radiation damage anisotropy consists of two sets of symmetry-equivalent reflections.

Introduction

Sequential measurement of integrated intensities is often accompanied by systematic change in the values of standard reflections measured at fixed exposure intervals. Indeed, a request for including the intensity variation observed throughout the diffraction experiment in papers reporting crystal structure determinations is to be found in the IUCr's *Notes for Authors* (1983). The observed variation in standards is