Acta Cryst. (1976). A**32**, 1010

Structure factor determination in α-ZrO_2 using the critical voltage effect. A comment.*

By M. David, R. Serneels† and R. Gevers‡, *Rijksuniversitair Centrum Antwerpen, Middelheimlaan* 1, 2020 *Antwerpen, Belgium*

(*Received* 5 *May* 1976; *accepted* 27 *May* 1976)

For the refinement of a systematic two-, three-, ... beam system, the higher-order reflexions to be considered should be carefully chosen. In particular for calculations on the second-order critical voltage effect (C.V.E.), the system **0**,**g**,2**g**, should be extended to a $(2N+1)$-beam system containing the reflexions $-(N-1)\mathbf{g}$ to $(N+1)\mathbf{g}$. Another choice (*e.g.* the system $-N\mathbf{g}$ to $N\mathbf{g}$) may lead here to serious errors unless N is very large.

In a recent paper concerning the second-order C.V.E., David, Gevers & Serneels (1975) have shown analytically that higher-order systematics, when properly taken into account may cause a shift of V_c (generally small), but do not influence the nature of the effect. This seems to contradict earlier numerical calculations on the C.V.E. in α-ZrO_2 by Ploc & Miller (1974). They made three-, five- and nine-beam calculations around V_c considering the reflexions 000 to 004 (three beams), $00\bar{4}$ to 004 (five beams) and $00\bar{8}$ to 008 (nine beams) with 004 in exact Bragg position. Their results seemingly indicated that the well-known discontinuous exchange of the excitation coefficients of Bloch waves (2) and (3) would occur only in the three-beam case and that, when the other systematics are present, V_c can only be defined as the voltage where the separation between the branches (2) and (3) of the dispersion surface is minimal. The purpose of the present comment note is to show that these anomalies are actually due to an inadequate choice of the reflexions to be considered.

We consider first the five-beam case. In addition to the three-beam system Ploc & Miller took $00\bar{2}$ and $00\bar{4}$ into account but omitted 006 and 008. However, the reflexions 006 and $00\bar{2}$ for instance are equally important since, because of the symmetry in the second-order Bragg orientation, they have the same excitation errors and they are coupled to the three-beam system by the same scattering factors. Moreover the beam $\mathbf{k}_0+\mathbf{g}_{00\bar{2}}$ ($\mathbf{k}_0$: wavevector of incident electrons) is then in exact Bragg orientation for scattering in the direction $\mathbf{k}_0+\mathbf{g}_{006}$. Similarly the reflexions $00\bar{4}$ and 008 are equally important. Thus, for five-beam calculation the reflexions $00\bar{2}$ and 006 should have been considered simultaneously. The same reasoning holds, of course, for the seven-, nine-, ... beam case. Generally in fact, to a systematic many-beam case with $s\mathbf{g}$ in (or close to) the Bragg position, higher-order systematics should be added in pairs of the form $[-r\mathbf{g},(r+s)\mathbf{g}]$, $r=1,2\ldots$.

Since the presence of a degeneracy in the dynamical system is likely to enhance all kinds of anomalies, one expects C.V. calculations to be particularly sensitive to an inconsistent choice of higher-order reflexions. The consequences in this case are in fact the following.

Consider a linear $(2N+1)$-beam system $[-(N-1)\mathbf{g}$ to $(N+1)\mathbf{g}]$ with 2**g** in exact Bragg position at V_c. Gevers, David & Serneels (1975) have shown that, when the system is coupled to a system of weak beams, a new degeneracy will occur at a slightly different voltage; it will, however, not any longer occur in the exact Bragg orientation unless

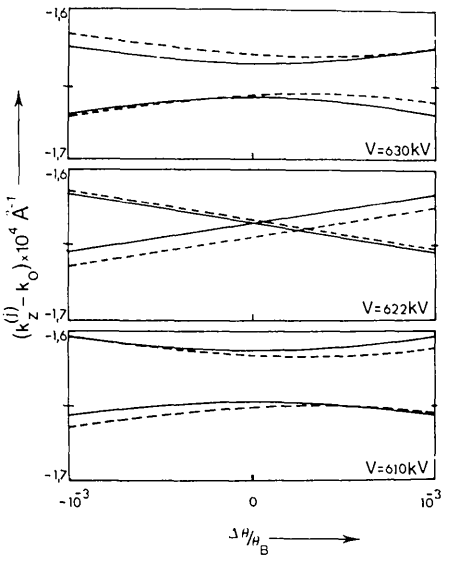

Fig. 1. The variation with voltage of the branches (2) and (3) of the dispersion surface close to the 222 Bragg orientation, for the nine-beam systems $\bar{3}\bar{3}\bar{3}$ to 555 (full lines) and $\bar{4}\bar{4}\bar{4}$ to 444 (dashed lines) in Al. The parameter $\Delta\theta/\theta_B$ (θ_B: 222 Bragg angle) represents the relative angular deviation from the exact Bragg orientation. In all calculations Smith & Burge (1962) potentials were used without a Debye-Waller correction.

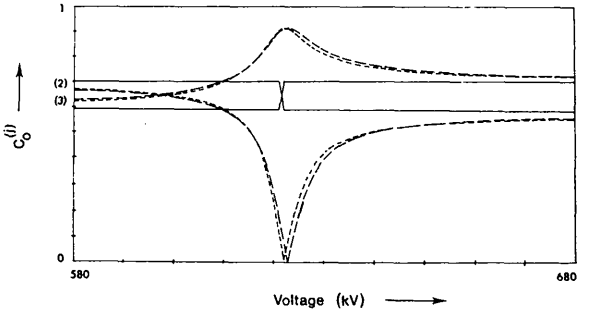

Fig. 2. The voltage dependence in Al of the Bloch-wave excitation amplitudes $C_0^{(2)}$ and $C_0^{(3)}$ for the nine-beam systems $\bar{3}\bar{3}\bar{3}$ to 555 (full lines) and $\bar{4}\bar{4}\bar{4}$ to 444 (short-dashed lines) with 222 in exact Bragg orientation. The long-dashed curves were obtained by considering the system $\bar{3}\bar{3}\bar{3}$ to 555 at a small deviation from the Bragg orientation, given by $\Delta\theta/\theta_B\simeq-3{\cdot}25\ 10^{-4}$.

* Work performed under the auspices of the association RUCA–SCK.

† Presently at L.U.C., Diepenbeek.

‡ Also at S.C.K., Mol.

the additional system has the same symmetry as the original one. The many-beam systems studied by Ploc & Miller will therefore be degenerate at some non-zero misorientation, as is illustrated in Fig. 1 for the Al 111 systematic row.

In the first place this explains why Ploc & Miller found only a minimizing of the separation between the two branches, since their computations were run under the exact Bragg condition. It also accounts for the anomalous behaviour of the excitation amplitudes they showed: this must be similar to the behaviour in the correct systematic case for a small misorientation, as illustrated in Fig. 2. The proof of the latter assertion requires a renormalized perturbation calculation and will be given in a later paper on the influence of non-systematic reflexions. The latter are expected to cause the same qualitative effects as inadequate higher-order systematics since in both cases the symmetry of the dynamical system is broken. We may thus conclude that the results of Ploc & Miller are irrelevant for the purely linear C.V.E.

The use of an inadequate many-beam system for numerical calculations on the C.V.E. is not unique in the literature. Usually a very large number of reflexions are used so that the errors introduced become negligible [see, for example, Metherell & Fisher (1969)]. Practically correct results are then obtained, however, only at the expense of a large computer time. The problem we have commented on here illustrates, moreover, the danger of drawing conclusions from numerical calculations alone without a thorough analytical understanding of a problem to guide them.

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Acta Cryst. (1976). **32**, 1011

A test on the statistics of derived intensities*.

By G. DE WITH and D. FEIL, *Chemical Physics Laboratory, Twente University of Technology P.O. Box* 217, *Enschede, The Netherlands*

(*Received* 7 *May* 1976; *accepted* 31 *May* 1976)

Variances of X-ray reflexions calculated with the procedure as proposed by McCandlish, Stout & Andrews [*Acta Cryst.* (1975), A**31**, 245–249] have been tested against variances determined in an independent way. A satisfying agreement is obtained.

On theoretical grounds one expects the variance σ^2 of an X-ray reflexion to be equal to the total number of counts T:

$$\sigma^2(I) = T. \tag{1}$$

I represents the number of net counts. As is well known the variance derived in this way does not represent sufficiently all errors. A term proportional to I^2 is often included:

$$\sigma^2(I) = T + F^2 I^2. \tag{2}$$

Several rationalizations have been given (McCandlish, Stout & Andrews, 1975).

The factor F is commonly chosen between 1×10^{-2} and 5×10^{-2} in an empirical way. To give some background to equation (2) a discussion of the variance has been given by McCandlish *et al.* (1975). They considered instrumental instability and data scaling. The following formula was derived:

$$\sigma^2(I) = K^2 T + S^2(K) I_o^2 + K^2 P^2 I_o^2 \tag{3}$$

where K is the scaling factor (or function), I_o the observed net intensity, I the real net intensity, $S^2(K)$ the variance of K and P the instability factor which can be estimated from reference reflexions.

A P value of 4×10^{-3} to 8×10^{-3} has been reported by McCandlish *et al.* (1975) for their card-controlled Picker diffractometer. To test this formula an analysis of a recently measured X-ray data set of pyrazine (de With, Harkema & Feil, 1976) was carried out. Because in this data set each independent reflexion has been measured approximately seven times, (symmetry-related ones and partial repetition), it was possible to calculate for each reflexion an external variance. On the other hand, an estimate of the contribution of instrumental instability and scaling procedure to the variance could be made, due to repeated measurement of three reference reflexions.

The variance estimated with equation (1) (counting statistics only) was tested against the external variance using the χ^2 test at a 97·5% confidence level. Curve A in the figure shows the ratio R of the experimental χ^2 value to the expected χ^2 value as a function of $\sin(\theta)/\lambda$. The curve presented is a smoothed one, representing average values. Each average contained reflexions from equal parts of reciprocal space (as covered by the experiment), a part being roughly equivalent to 20 reflexions (the behaviour of the curve was largely independent of the exact number of reflexions in each part). This means that a significant difference is expressed in Fig. 1 as a ratio greater than one. As can be seen from the plot, differences are significant upto $\sin(\theta)/\lambda = 0{\cdot}75$ Å^{-1}. This indicates once again that counting statistics alone do not represent properly the variance of a reflexion.

* This research has been carried out under the auspices of the Foundation for Fundamental Research on Matter by Electron and X-rays (FOMRE) and with aid from the Netherlands Organization for Advancement of Pure Research (ZWO).