Table 1. *Revised frequencies for* 53 *space groups*

Not including 12 unoccupied space groups.

Space group	Number	Revised frequency	Space group	Number	Revised frequency
$P1$	1	610	$I4_322$	98	2
$P2$	3	22	$P3$	143	20
$P2_1$	4	3914	$P3_1$	144	31
$C2$	5	546	$P3_2$	145	31
$P222$	16	14	$R3$	146	80
$P222_1$	17	18	$P321$	150	10
$P2_12_12$	18	374	$P3_121$	152	35
$P2_12_12_1$	19	6718	$P3_221$	154	35
$C222_1$	20	172	$R32$	155	46
$C222$	21	10	$P6_1$	169	30
$I222$	23	14	$P6_5$	170	30
$I2_12_12_1$	24	10	$P6_2$	171	5
$P4$	75	2	$P6_4$	172	5
$P4_1$	76	54	$P6_3$	173	66
$P4_2$	77	6	$P622$	177	4
$P4_3$	78	54	$P6_122$	178	7
$I4$	79	24	$P6_522$	179	7
$I4_3$	80	18	$P6_222$	180	5
$P422$	89	2	$P6_422$	181	5
$P42_12$	90	8	$P6_322$	182	12
$P4_122$	91	4	$I23$	197	6
$P4_12_12$	92	145	$P2_13$	198	30
$P4_222$	93	4	$F432$	209	2
$P4_22_12$	94	14	$F4_132$	210	6
$P4_322$	95	4	$P4_332$	212	2
$P4_32_12$	96	145	$P4_132$	213	2
$I422$	97	4			

Table 2. *The* 12 *space groups with the highest frequencies*

Space group	Number of entries	Percent of total	Space group	Number of entries	Percent of total
$P2_1/c$	10450	29·2	$P1$	610	1·7
$P2_12_12_1$	6718	18·8	$Pnma$	548	1·5
$P\bar{1}$	3986	11·1	$C2$	546	1·5
$P2_1$	3914	10·9	$Pna2_1$	513	1·4
$C2/c$	1930	5·4	$P2_12_12$	374	1·0
$Pbca$	1261	3·5	$Pbcn$	341	1·0

frequency of occurrence for each of the 230 space groups. This file is based on structures that have been reported in the literature.

However, for some compounds a space-group determination has an added bonus in that a second space-group determination is automatically made. Thus, when Shoemaker, Schomaker, Donohue & Corey (1950) established the space group of L-threonine as $P2_12_12_1$ they automatically established the space group of D-threonine also as $P2_12_12_1$, without ever seeing any of that substance. On the reasonable assumption that, because we are concerned here with organic molecules, all of the 3359 crystals in the file that were found to have space group $P2_12_12_1$ will have a corresponding enantiomer with that space group, so the frequency should be doubled. This same situation will obtain for the other 64 space groups that contain no symmetry operations of the second kind. These are those space groups belonging to point groups 1, 2, 222, 4, 422, 3, 32, 6, 622, 23 and 432. In the case of the ten enantiomeric pairs, for example, $P4_1$ and $P4_3$, for which 47 crystals were found for the former, and seven for the latter, the results should be combined, to give 54 for each for that pair; similar calculations were made for the other nine pairs. For the remaining space groups the number of entries should be doubled. The revised frequencies are presented in Table 1. This table should be combined with the unrevised values of Table 1 of Mighell *et al.* to give the complete set of frequencies for the 230 space groups. The total number of crystals is increased from 29 059 to 35 771.

In the unlikely event that two different sets of investigators reported determinations, say, of D-tartaric acid in one laboratory and L-tartaric acid from a second laboratory, the space group for both will already be in the file, and the frequency number for $P2_1$ will be over-revised. I believe that the chance that this has happened is very small indeed.

The rank order of the first five most populous space groups is changed, with $P2_12_12_1$ now in second place instead of $P\bar{1}$. The first 12 in the list are presented in Table 2. Each of the remaining 218 space groups has less than 1% of the total.

The precautionary remarks of Mighell *et al.* still, of course, apply.

I thank Dr Richard E. Marsh for interesting suggestions.

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A comment on the calculation of rocking curves near the critical voltage in electron diffraction.

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(*Received* 12 *March* 1984; *accepted* 10 *October* 1984)

Abstract

Several authors have reported the occurrence of a sharp peak doublet in certain rocking curves calculated for voltages near the critical voltage in electron diffraction. It is shown that such peaks are only artefacts due to the use of an approximation that becomes invalid under illumination conditions for which the main Bloch waves are nearly degenerate.

0108-7673/85/020204-03$01.50

Sellar, Imeson & Humphreys (1980) have published numerically calculated rocking curves of the 2**g** diffracted intensity ($I_{2\mathbf{g}}$) when an electron beam is incident on a crystal foil oriented so that only systematic reflections $n\mathbf{g}$ are important (**g**: reciprocal- lattice vector), the accelerating voltage being very close to the 'second-order critical voltage'. They reported, among other things, the occurrence of two sharp intensity peaks at orientations very close to the second-order Bragg orientation and positioned symmetrically with respect to the latter. Such peaks have never been observed. Sellar *et al.* attribute this to the extreme narrowness of the peaks.

Stumpp (1983) obtained similar curves at a third-order critical voltage, but he supposed that the peaks were mathematical artefacts since they do not appear if certain reasonable sets of absorption potentials are taken into account.

We wish to point out here that such peaks actually do not exist: their occurrence in certain calculated rocking curves is due to the use of an expression for the diffracted amplitudes [see *e.g.* Sellar *et al.*, 1980, equation (2)], which is erroneous when absorption is taken into account.

The wavefunction in the crystal, the Bloch waves and the amplitude of the diffracted beams are given by, respectively,

$$\psi(\mathbf{r})=\sum_j c_j\varphi_j(\mathbf{r}),\quad \varphi_j(\mathbf{r})=\sum_n C_n^j \exp i2\pi(\mathbf{k}^j+n\mathbf{g})\,.\,\mathbf{r} \qquad (1a)$$

$$\psi_{n\mathbf{g}}(z)=\sum_j c_jC_n^j \exp i2\pi k_z^j z \qquad (1b)$$

(z: depth under the entrance surface), where C_n^j, $n=0,1,\ldots$, are the components of the jth eigenvector of the well known 'dynamical matrix' while the 'excitation coefficients' c_j are found from

$$\sum_j c_jC_n^j=\delta_{n0}. \qquad (1c)$$

Without absorption the Bloch waves are orthonormal:

$$\sum_n C_n^{j*}C_n^k=\delta_{jk}, \qquad (2a)$$

whence

$$c_j=C_0^{j*}. \qquad (2b)$$

However, when absorption is taken into account phenomenologically by adding a small imaginary term $iV'(\mathbf{r})$ to the crystal potential $V(\mathbf{r})$, then (2) does not hold any more. As a matter of fact, the origin of reciprocal space being chosen so that the Fourier coefficients $V_{n\mathbf{g}}$, $V'_{n\mathbf{g}}$ of $V(\mathbf{r})$, $V'(\mathbf{r})$ are real (see *e.g.* Serneels, David & Gevers, 1975), the dynamical matrix with absorption is still symmetric ($S=\tilde{S}$) and it is easily seen, using some matrix algebra, that (1c) then yields

$$c_j=C_0^j/[\sum_n (C_n^j)^2], \qquad (3)$$

where c_j may still be interpreted as an 'excitation coefficient' if the eigenvectors of the dynamical matrix are normalized to one, *i.e.* $\sum_n |C_n^j|^2=1$.

David, Gevers & Serneels (1976, 1977) have discussed at length the influence of absorption on the critical voltage effect for a systematic row, treating the term $iV'(\mathbf{r})$ as a perturbation. It was found that ordinary degenerate perturbation theory led to divergences due to the non-hermitian character of the dynamical matrix S when absorption is included. The divergences could be overcome by 'straining' the parameters representing the illumination conditions (*i.e.* a form of renormalization of the perturbation series). As a result it could be shown that the critical voltage V_c is slightly shifted due to the absorption, that there is a twofold degeneracy at V_c for *two* orientations extremely close and symmetrical with respect to the exact 2**g** Bragg orientation, and that the dynamical matrix is non-diagonalizable at these degeneracies (*i.e.* its Jordan canonical form contains a non-zero nilpotent). The latter implies that the eigenvectors of S corresponding to the twofold degenerate eigenvalue collapse.

Furthermore, it was shown that, under illumination conditions close to the 'critical' ones, the latter eigenvectors (denoted by, say, X_2, X_3) can be expressed *exactly* in the form

$$X_2=\cos\Phi Y\mp\sin\Phi Z,\qquad X_3=\mp\sin\Phi Y-\cos\Phi Z, \qquad (4)$$

where Y and Z are vectors that remain practially constant when the illumination conditions are slightly varied, while the *complex* angle $\Phi=\Phi'+i\Phi''$ may vary drastically and accounts completely for the singular behaviour of X_2 and X_3 at the degeneracies. In fact it is a very good approximation to replace Y and Z in (4) by the eigenvectors that would correspond to the degenerate eigenvalue if absorption were neglected. The leading contribution to the amplitude $\psi_{2\mathbf{g}}$ [which comes from $\varphi_2(\mathbf{r})$ and $\varphi_3(\mathbf{r})$] can then be written as

$$\begin{aligned}\psi_{2\mathbf{g}}^{(2,3)}&=[\exp i\pi(k_z^2+k_z^3)z][a\cos\pi\sigma z\\&\quad+(b\cos 2\Phi+c\sin 2\Phi)\sin\pi\sigma z],\\ \sigma&=k_z^2-k_z^3,\end{aligned} \qquad (5)$$

where a, b and c are nearly constant [$O(|a|)=0{\cdot}1$, $O(|b|,|c|)=1$].† On the other hand, if (2b) is used instead of (3) one finds an expression of the form

$$\begin{aligned}\psi_{2\mathbf{g}}^{(2,3)}=[\exp i\pi(k_z^2+k_z^3)z]\bigg[&(a+ia'\tanh 2\Phi'')\cos\pi\sigma z\\&+\frac{b\cos 2\Phi'+c\sin 2\Phi'}{\cosh 2\Phi''}\sin\pi\sigma z\bigg],\end{aligned} \qquad (6)$$

where $a'\simeq 2$. It is clear that (5) and (6) would be the same if Φ were real. From the expression for Φ'' derived by David *et al.* (1977), one can see that putting $\Phi''=0$ is in fact an acceptable approximation except, however, in a very narrow voltage and orientation interval around the conditions for degeneracy ($\sigma=0$). At the degeneracies Φ'' becomes infinite (describing the collapse of X_2 and X_3) and the second term in (5) becomes a limit $0\times\infty$. Expression (6) then gives entirely different values and leads in particular to the erroneous sharp peak doublet shown by Sellar *et al.* Moreover, it can be verified that the position of those peaks, for voltages up to 5 or 10 kV away from the critical voltage, does correspond to a maximum of Φ'', as expected from (6). The same arguments apply for higher-order critical voltage effects.

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† $O(|x|)\equiv$ the order of magnitude of x.

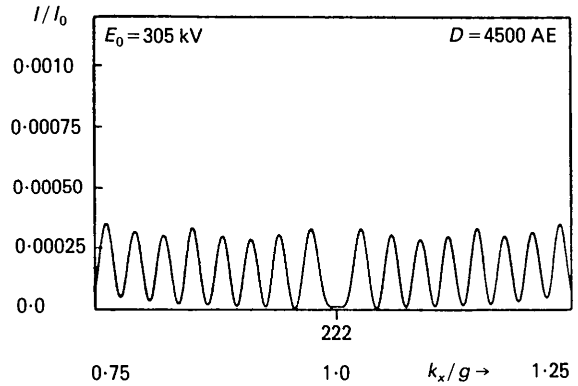

Fig. 1. Calculated rocking curve (temperature 356 K) for copper 111; seven-beam calculation ($\bar{2}\bar{2}\bar{2}, \ldots, 444$). $V_{000} = 16{\cdot}00$, $V_{111} = 11{\cdot}68$, $V_{222} = 5{\cdot}28$, $V_{333} = 2{\cdot}63$, $V_{444} = 1{\cdot}25$, $V_{555} = 0{\cdot}61$, $V^{\rm I}_{000} = 1{\cdot}50$, $V^{\rm I}_{111} = 0{\cdot}74$, $V^{\rm I}_{222} = 0{\cdot}46$, $V^{\rm I}_{333} = 0{\cdot}38$, $V^{\rm I}_{444} = 0{\cdot}22$, $V^{\rm I}_{555} = 0{\cdot}11$.

We therefore believe that the anomalous peaks predicted by Sellar *et al.* (1980) are mathematical artefacts. The form of the main contribution to I_{2g} near the critical voltage *does not* differ from 'the usual shape-transform type', as follows from (5) and from the fact that both $\cos 2\Phi$ and $\sin 2\Phi$ are proportional to σ^{-1}. Fig. 1 shows a calculated rocking curve that agrees very well with their experimental results.

The authors wish to thank Dr H. Matsuhata for a stimulating discussion.

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