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AUSTRALIAN NUCLEAR SCIENCE AND TECHNOLOGY ORGANISATION

LUCAS HEIGHTS RESEARCH LABORATORIES

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ABSTRACT

The interplanar spacings and intensities of all lines appearing in the X-ray powder diffraction pattern of perovskite have been calculated. Many of the lines occur in groups with a large amount of overlap. As an aid to identifying the lines which are observed, the intensity profiles of the major groups have been plotted. Those lines which are relatively free of overlap and can be identified unambiguously have been used to calculate the lattice parameters, with the results $a = 5.4424 \pm 0.0001$ Å, $b = 7.6417 \pm 0.0002$ Å, $c = 5.3807 \pm 0.0001$ Å.

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CUBIC LATTICES; LATTICE PARAMETERS; POWDERS; OXIDE MINERALS; X-RAY DIFFRACTION

EDITORIAL NOTE

The Australian Nuclear Science and Technology Organisation replaced the Australian Atomic Energy Commission on 27 April 1987. Reports issued after April 1987 have the prefix ANSTO with no change of the symbol (E, M, S or C) or numbering sequence.

CONTENTS

1. INTRODUCTION

Perovskite is one of the three major phases of Synroc, a synthetic rock that has been proposed as a matrix for immobilising high-level radioactive wastes [Ringwood *et al.* 1979]. There is, therefore, considerable interest in knowing how it responds to irradiation, and changes in the lattice parameters provide a means of monitoring change in its structural state. Unfortunately, measurement of the lattice parameters is not entirely straightforward. The diffraction patterns of perovskite obtained with either copper Kα or cobalt Kα radiations contain several lines at high angles ($2\theta > 120°$), which are suitable for accurate determination of lattice parameters, provided they can be indexed. Herein lies the problem.

The diffraction pattern of perovskite consists mainly of groups of closely spaced lines, many of which overlap one another. In such cases calculation of the expected angular position of a line is not sufficient to identify it with certainty; it is also necessary to know the relative intensities of all lines which occur close to the observed angle. Information on intensities is given, together with interplanar spacings (d values), for each material in the JCPDS data file, but the entry for perovskite contains no information on lines for which $d < 0.899$ Å, and some of the lines of interest when using copper Kα radiation have $d \sim 0.78$ Å. We have, therefore, calculated the intensities and d values of all lines that might appear in a diffraction pattern when using either copper or cobalt Kα radiations.

However, particularly at high angles where the α1 and α2 components of a line are clearly resolved, it is not easy to identify the lines that are actually observed simply by inspection of a list of intensities and d values. We have, therefore, also plotted intensity profiles for the major groups of lines with $2\theta > 80°$. Inspection of these profiles indicates which lines are most suitable for a measurement of lattice parameters.

The greatest accuracy can be obtained by matching computed profiles with digital diffractometer data but, for reasons to be explained, we have used film techniques and rely on visual identification of lines. This technique is more restrictive in the lines that can be used, and some of our later discussion refers only to this technique. However, it should be noted that with chart recorder output from a diffractometer, as commonly used, it is very easy to identify incorrectly some of the lines that are observed. Comparison of diffractometer traces with calculated intensity profiles should ensure that errors of identification are not made.

Rather surprisingly, our calculations showed that there were several errors of indexing, involving some of the strongest lines, in the entry for perovskite in the JCPDS data file. Although the strong, low-angle lines are not ideal for determination of lattice parameters, in heavily irradiated material they are the only lines that can be distinguished. We have, therefore, thought it worthwhile to publish our interpretation of the full pattern.

Two careful determinations of the lattice parameters of perovskite have already been published, with very significant differences between the results [Kay and Bailey 1957, Swanson *et al.* 1971]. These differences may be due to differences in purity, but since we do not know which, if either, of the materials previously investigated matches the purity of the material used for preparation of Synroc and its constituent minerals at the Lucas Heights Research Laboratories in recent years, we have made a careful measurement of the lattice parameters of a representative sample of this perovskite.

2. THE POWDER DIFFRACTION PATTERN CALCULATIONS

2.1 The Structure of Perovskite

The ideal perovskite structure is shown in **figure 1**. The unit cell is cubic with one formula unit, $CaTiO_3$, per cell. Perovskite itself has a distorted perovskite structure, with orthorhombic symmetry [Kay and Bailey 1957]. The relation between the orthorhombic and pseudo-cubic unit cells is shown in **figure 2**. The magnitude of the shear distortion of the cubic sub-cell is quite small, ~ 48′, and the general appearance of the powder diffraction pattern can be understood by reference to this cell.

Owing to the structural distortion, each line that would appear if the structure were truly cubic is split into a group of lines, with interplanar spacings that differ by $\lesssim 1\%$. The indices of any line referred to the orthorhombic unit cell, hkl, can be obtained from its indices referred to the cubic unit cell, h′k′l′, by matrix multiplication, *i.e.*

$$\begin{pmatrix} h \\ k \\ l \end{pmatrix} = \begin{pmatrix} 1 & 0 & \bar{1} \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{pmatrix} \begin{matrix} h' \\ k' \\ l' \end{matrix}$$

Thus 111 becomes 022 and $11\bar{1}$ becomes 220, with a slightly different *d* spacing.

Since the distortion is small, the structure factors of all lines in a group are approximately equal, and their relative intensities are determined mainly by their multiplicities. This does not apply to lines which are not derived from crystallographically equivalent lines of the cubic sub-cell, *i.e.* lines for which h′, k′ or l′ are not integral and for which the intensity would be zero but for the orthorhombic distortion. Some such lines have *d* values which cause them to appear within a group of related lines. Note that the sum of the multiplicities of all related lines in a group must equal the multiplicity of the (cubic) line from which they are derived. This provides a simple means of checking that all lines in a group have been considered.

The pseudo-cubic unit cell is primitive, but the pattern of sites of the two heaviest atoms in the cell, Ca and Ti, which are of almost equal scattering power, is body centred. Consequently the reflections for which h′ + k′ + l′ is even are much stronger than those for which it is odd. Reflections for which h′, k′ or l′ are non-integral are generally weaker still, but there are some significant exceptions to this rule, particularly at high angles.

These predictions were confirmed by detailed calculations based on the atomic parameters of the orthorhombic structure.

2.2 Interplanar Spacings and Intensities

The space group of perovskite is No. 62. The structural parameters were first determined by Kay and Bailey [1957], and more recently by Koopmans *et al.* [1983]. Both these sets of authors used the setting Pcmn, but for ease of comparison with the powder diffraction work of Swanson *et al.* [1971], on which the entry in the JCPDS data file is based, we have used Pnma, which is the setting in the International Tables for X-ray Crystallography [1965].

We have calculated the intensities and *d* values of all lines in the patterns obtained with Cu Kα or Co Kα radiations, using the atomic parameters of Koopmans *et al.*, the lattice parameters of Swanson *et al.* corrected as described in **section 3.4**, and the atomic scattering factors of Doyle and Turner [1968]. **Table 1** lists the results for Cu Kα and Co Kα radiations for all lines for which the intensity with Cu radiation is greater than 0.4 per cent of that of the strongest line, and some weaker lines where

(a) the line is close enough to another line that meets the intensity criterion for the pair not to be resolved, and may be strong enough to affect significantly the observed position of the combined line; or

(b) the combined strength of two or more closely overlapping lines of comparable strength is greater than 0.4 per cent of that of the strongest line.

These criteria appear to match fairly closely the limits of visibility encountered by Swanson *et al.*

The intensities listed are those of the Cu Kα1 component of a line. Since in practice the α1 and α2 components of the reference line, 121, are not resolved, the observed relative intensity of the α1 component of a line that is resolved will be approximately two-thirds of the tabulated intensity, and the intensity of the α2 component will be approximately half that of the α1. For the few lines with $\theta_b > 80°$ (θ_b is the Bragg angle), the difference between the Lorentz polarisation factors for the α1 and α2 components of a line may be significant.

Also listed in **table 1** are the $2\theta_b$ values for Cu and Co Kα1 and Kα2 radiations. Both α1 and α2 values are needed to identify overlapping lines, particularly at high angles.

For lines with $d > 1.1$ Å, the intensity with Co Kα radiation is nearly the same as the intensity with Cu Kα radiation. For lines with $d < 1.1$ Å, the Lorentz polarisation factor, and hence the intensity, are significantly greater with Co radiation. The difference amounts to a factor of about four for the 315 line, and is even greater for lines at higher angles, but it is unlikely that any lines would be seen with Co radiation other than those listed in **table 1**.

2.3 Identification of Lines

Inspection of the data in **tables 1** and **2** should enable groups of overlapping lines to be interpreted. Interpretation is much simpler, however, if the calculated intensity profile of a group is compared with the appearance of a film. We have calculated the intensity profiles for the prominent high-angle groups of lines in diffraction patterns taken with copper Kα and cobalt Kα radiations, with the results shown in **figures 3** to **13**.

When calculating the intensity profiles, the shape of an individual line was assumed to be Gaussian. The width parameter was chosen so that the calculated profile roughly matched the appearance of a group of lines. The same value was used for all lines in a group but different values were used for different groups, the width of a line increasing with increase in θ. Enlarged prints of the major groups of lines are shown in **figures 14** and **15**. These can be compared with the calculated profiles shown in **figures 3** to **13**.

2.4 Choice of Lines

Inspection of **figures 3** to **13** shows that there are a few high-angle lines that are clearly resolved from all other lines. None of them is a very strong line, but nevertheless they are the lines of first choice and in some cases are adequate for a determination of the lattice parameters. Mostly they are α1 components of lines at the low angle side of a group, *e.g.* 521, 600, 523, 602, 640 and 642, and unfortunately none of them is very sensitive to the values of *b* or *c*. As a result, the set of equations obtained by using only these lines is not particularly well-conditioned, and accuracy can be improved by including some other lines that are more sensitive to *b* and *c*.

The question of which other lines can be used without introducing unacceptable errors is not easily answered. Clearly, if two lines were to fall at exactly the same angle, the observed position of the line could be used for each of them with no greater error than if the line had been single. Exact coincidences, unfortunately, do not occur, and in practice it has to be decided whether the width of a composite line indicates that its components are so close together that they may be assumed to be coincident. In this connection the following points should be noted :

(a) The random error in locating a peak position is ~0.04°(2θ), which is much less than the width of a peak, particularly at high angles. If the components of a double line are of equal intensity and are separated by as little as 0.1°(2θ), broadening of the line will not be conspicuous yet the error in assuming that the lines are coincident may be significant.

(b) Where the components of a line are of widely differing intensity, the peak position will be dominated by the position of the strongest component. Provided that the line is not obviously broadened, the peak position may be assumed to be the position of this component, but not of the other components.

Figures 3 to **13** are, of course, drawn for one particular set of values of the lattice parameters and line widths, and will change in detail if these values are changed. It should not be assumed, therefore, that overlapping lines which appear to be acceptable on the basis of one of these figures, *e.g.* 642(α2) and 480(α1) (Δ2θ=0.01°), will necessarily be acceptable with an irradiated specimen for which the parameters are different. Conversely, there may be lines which do not appear to be acceptable according to **table 1**, but which nevertheless could be used. The only safe course is to check with each specimen that any overlapping lines which have been used in the analysis are not the source of unacceptable errors.

It is fortunate that neutron irradiation changes the lattice parameters in such a way as to spread out the lines within each group, thereby improving the resolution of lines at the sides of the group [Ball *et al.* 1988]. Unfortunately, neutron irradiation also broadens and weakens all lines, particularly those at high angles. In heavily irradiated specimens all detail is lost within the high-angle groups and the best estimates of lattice parameters are obtained using isolated, low-angle lines and overlapping lines such as 323, 161, 404 and 080, which normally would not be acceptable. Inevitably, the accuracy attainable with such specimens is not as good as with non-irradiated material.

3. LATTICE PARAMETER MEASUREMENTS

3.1 Sample Preparation

Perovskite was made by ball-milling equi-molar amounts of TiO_2 and $CaCO_3$ in alcohol, using zirconia balls, followed by drying, compacting and calcining in a reducing atmosphere (N_2/3.5% H_2) at 1100 °C for 16 hours. The material was then powdered, compacted and sintered at 1300°C in air for a further 16 hours.

The starting materials were of commercial purity, nominally 99.5 per cent. The calcined material was analysed by inductively coupled plasma (ICP) spectroscopy, with the results shown in **table 2**. Presumably the zirconium came from the zirconia balls used for ball-milling, so the amount is likely to vary from one batch to the next. Scanning electron microscopy of sintered material revealed some very small particles that were rich in zirconium, indicating that not all of the zirconium reported in **table 2** was actually in solution in perovskite. It was not possible to obtain a reliable analysis of the perovskite itself by this means. The zirconium-rich phase was not detected by X-ray diffraction, which showed only perovskite.

3.2 X-ray Examination

Specimens for X-ray examination were prepared by mixing a small amount of powdered perovskite with an approximately equal amount of gum tragacanth, moistening with water and rolling to a rod of diameter ~0.2 mm. This was mounted in a 114.3 mm diameter powder camera (Philips type PW1024), and irradiated with Cu Kα or Co Kα radiation. The same specimen, which was not moved between exposures, was used for both radiations. Systematic errors arising from camera geometry should therefore be the same for both films. There may be differences due to the different rates of absorption of Cu and Co radiations in the specimen, but we expect that any such differences will be negligible.

The scattered radiation was filtered through ~0.04 mm of aluminium (three thicknesses of cooking foil) to reduce the intensity of fluorescent radiation from titanium and calcium relative to the primary radiation, and recorded on Agfa D7p X-ray film. Exposure times were ~20 hours for copper radiation or ~40 hours for cobalt radiation. The X-ray equipment is housed in an air-conditioned room, but no other precaution was taken to ensure a constant temperature. Temperature variation during an exposure may have been as much as ±2°C from the controlled temperature of 25°C.

Measurements of line position were made with a Hilger and Watts film measuring rule reading to 0.05 mm. The usual correction was made for film shrinkage, which also allowed for the fact that, with one thickness of aluminium foil behind it, the film was not in direct contact with the camera body.

The estimated standard deviation in a measurement of $2\theta_b$ is approximately 0.04° in our work. Peak positions can be measured much more precisely than this with a diffractometer, but peak positions must be corrected for several systematic errors before $2\theta_b$ values of comparable accuracy can be obtained; in general $2\theta_b$ values obtained with a diffractometer are subject to errors of the same magnitude as with a film. However, our reasons for using a camera were that, with neutron irradiated specimens, there is an incentive to use very small amounts of material, and that, with a diffractometer, the maximum accessible value of 2θ is ~160°, whereas with perovskite several lines occur at higher angles.

It is true that the angular resolution obtainable with a diffractometer is generally better than with a camera, but this advantage is less pronounced at high angles where line widths are dominated by specimen parameters. Also, although diffractograms can be obtained with very small amounts of material, the time required to record a set of broad and weak high-angle lines is very long.

3.3 Results

Four sets of measurements were made on each of two films (one each with copper and cobalt radiations). The mean value of 2θ for each of the lines chosen for calculation of the lattice parameters is given in **table 3**, together with an estimate of its accuracy based on the scatter of the individual measurements.

The scatter of the estimated standard deviations (e.s.d.) is partly due to the small number of measurements of each line, and partly to inherently better accuracy in the measurement of some lines. It should be noted that the measuring rule was read only to the nearest 0.05 mm when recording the position of a line, which is equivalent to 0.05° in 2θ, and that the positions of two lines must be recorded to obtain one value of $2\theta_b$. Estimates of uncertainty that are 0.02° or less should therefore be treated with caution. However, the e.s.d. values of high-angle lines ($2\theta > 140°$) seem to be significantly greater than those of low-angle lines ($2\theta < 125°$), which reflects the difficulty experienced in setting the cursor of the film measuring rule on a very weak or broad line. The mean e.s.d. of low-angle lines is 0.023 ± 0.010°, and that of high-

angle lines is 0.044 ± 0.017°. This would suggest that the ratio of the intrinsic weights of low- and high-angle lines should be 4:1. However, there is considerable uncertainty in the mean values of e.s.d. for the two groups of lines and, as stated earlier, there are reasons for supposing that some of the values of e.s.d., affecting mainly the low-angle lines, have been underestimated. We have, therefore, used weighting factors of two and unity.

The data were analysed using a program based on Hess's modification of Cohen's method [Klug and Alexander 1974], with the results shown in **table 4**. The systematic error, $\Delta\theta$, was assumed to obey the relation

$$\Delta\theta = K\,(1/\sin\theta + 1/\theta)\,\sin(2\theta),$$

where K is a drift constant. This is equivalent to assuming that

$$\Delta d/d = K\,(1/\sin\theta) + 1/\theta)\,\cos^2\theta.$$

In fact, the systematic error drift coefficient was very small, and essentially the same results were obtained assuming zero drift.

The quoted uncertainties in the lattice parameters are based on external estimates of error in the measurements of 2θ. Using the derived values of the lattice parameters we have calculated the apparent error in each measurement. The mean values of $|(2\theta_{calc}-2\theta_{obs})|$ for the low- and high-angle groups of lines are 0.029° and 0.041°, respectively, in very good agreement with the previous estimates from internal consistency, and confirm the choice of weighting factors.

Also shown in **table 4** are the lattice parameters obtained by Kay and Bailey [1957], by Swanson *et al.* [1971], and by re-analysis of some of the data of Swanson *et al.*

3.4 Discussion

The agreement between the first three sets of parameters listed in **table 4** is not good when the accuracy claimed by each group of authors is considered. However, before the significance of the difference can be assessed, it is necessary to consider what effect incorrect indexing may have had in the work of Swanson *et al.* [1971]. We have, therefore, re-analysed their data, including only lines which should have been free from interference by neighbouring lines and for which $2\theta > 78°$, with the results shown in **table 4**. The revised values of *b* and *c* are in good agreement with those of the present work, but the discrepancy between the values obtained for *a* may be significant. If so, it may be due to the zirconium in our material.

The parameters of Kay and Bailey [1957] are very different, especially the *c* parameter. It is tempting to attribute this to a difference in composition, particularly since Kay and Bailey noticed "slightly increased lattice parameters (>1.33%)" in some samples, which they attributed to the presence of Nb, Ta or Fe. Note that 1.33% is much greater than the discrepancy between their values and ours, which is less than 0.3 per cent. However, Kay and Bailey noted that the relative positions of lines were the same in specimens with normal and increased parameters, which would indicate that all three parameters had been changed by the same amount. None of the abnormal specimens, therefore, would have had parameters matching those of our material.

The fact that synthetic material and six naturally occurring crystals examined by Kay and Bailey had identical parameters suggests that these materials were pure. However, the synthetic materials prepared for Swanson *et al.* and by us were also moderately pure, apart from slight contamination by zirconium in our material, so it seems unlikely that the differences in lattice parameters can be attributed to differences in composition. Kay and Bailey determined their lattice parameters from powder photographs, but they did not say which lines were used in the analysis. They indexed their pattern using approximate values of the parameters obtained from single-crystal observations of natural material. This procedure, if not checked by calculation of line intensities, is very likely to lead to confirmation of the approximate values through incorrect indexing of high-angle lines and we think that this may be the explanation for the values of lattice parameters that they obtained.

4. CONCLUSIONS

The intensities and interplanar spacings have been calculated for all lines in the powder diffraction patterns (Cu and Co Kα radiations) of perovskite, down to $d = 0.772$ Å. The results for all lines that are likely to be observed in practice are given in **table 1**.

Intensity profiles have been drawn for the major groups of lines with $2\theta > 90°$. Inspection of these profiles shows that there is very substantial overlap between neighbouring lines in most major groups, and reveals which lines in these groups are relatively free of overlap and so suitable for determination of the lattice parameters.

The lattice parameters of a typical sample of perovskite made from standard materials have been determined. The results are given in **table 4.**

5. ACKNOWLEDGEMENTS

We are indebted to D.J. Cassidy for preparation of the sample of perovskite, D.M. Levins for the chemical analysis, K.G. Watson for examination of the perovskite sample by scanning electron microscopy, and J. Warmeant for preparing **figures 14** and **15.**

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TABLE 1

POWDER DIFFRACTION DATA FOR PEROVSKITE

Cu Kα = 1.54060 A, Cu Kα2 = 1.54443 A

Co Kα = 1.78903 A, Co Kα2 = 1.79289 A

		Copper Radiation			Cobalt Radiation		
h k l	d(A)	I	2θ°(α 1)	2θ°(α 2)	I	2θ°(α 1)	2θ°(α 2)
1 0 1	3.826	10.4	23.23	23.29	10.6	27.04	27.10
0 2 0	3.821	4.6	23.26	23.32	4.7	27.08	27.14
1 1 1	3.421	3.0	26.03	26.09	3.0	30.32	30.38
2 0 0	2.720	26.0	32.90	32.98	26.1	38.40	38.48
1 2 1	2.704	100.0	33.11	33.19	100.0	38.64	38.73
0 0 2	2.690	23.9	33.27	33.36	23.9	38.84	38.92
2 1 0	2.563	1.0	34.98	35.07	1.0	40.86	40.95
2 0 1	2.428	1.1	37.00	37.09	1.1	43.24	43.34
1 0 2	2.412	1.7	37.25	37.35	1.7	43.54	43.64
2 1 1	2.314	1.7	38.89	38.99	1.6	45.49	45.59
0 3 1	2.302	3.9	39.09	39.19	3.9	45.73	45.83
1 1 2	2.300	3.4	39.14	39.24	3.4	45.78	45.88
2 2 0	2.216	5.0	40.68	40.79	4.9	47.61	47.72
0 2 2	2.200	4.2	40.99	41.10	4.2	47.99	48.10
1 3 1	2.120	2.2	42.61	42.72	2.1	49.91	50.02
2 2 1	2.049	1.7	44.16	44.28	1.7	51.77	51.89
1 2 2	2.039	1.2	44.38	44.50	1.2	52.03	52.15
2 0 2	1.9129	43.6	47.49	47.62	42.4	55.76	55.89
0 4 0	1.9104	23.2	47.56	47.68	22.6	55.84	55.97
2 3 0	1.8593	1.6	48.95	49.08	1.6	57.51	57.65
2 1 2	1.8556	1.9	49.05	49.18	1.9	57.64	57.77
2 3 1	1.7574	0.6	51.99	52.13	0.6	61.20	61.34
1 3 2	1.7513	0.7	52.19	52.33	0.7	61.43	61.58
0 1 3	1.7462	0.4	52.35	52.49	0.4	61.63	61.78
3 0 1	1.7185	2.2	53.26	53.40	2.2	62.73	62.88
2 2 2	1.7105	1.9	53.53	53.67	1.8	63.06	63.21
1 4 1	1.7092	1.6	53.58	53.72	1.5	63.12	63.27
1 0 3	1.7035	0.5	53.77	53.91	0.5	63.35	63.50
3 1 1	1.6767	3.5	54.70	54.85	3.4	64.49	64.64
1 1 3	1.6627	0.7	55.20	55.35	0.7	65.10	65.25
3 2 1	1.5673	15.2	58.88	59.04	14.9	69.60	69.78
2 4 0	1.5634	10.3	59.04	59.20	10.1	69.80	69.97
0 4 2	1.5577	9.9	59.28	59.44	9.7	70.10	70.27
1 2 3	1.5559	22.2	59.35	59.51	21.7	70.19	70.36
1 4 2	1.4975	0.15	61.91	62.08	0.14	73.36	73.54
2 0 3	1.4974	0.25	61.92	62.09	0.25	73.36	73.55
0 5 1	1.4702	0.5	63.19	63.37	0.5	74.95	75.14
3 3 1	1.4246	1.3	65.46	65.65	1.3	77.79	77.99
4 0 0	1.3601	4.2	68.99	69.19	4.3	82.25	82.46
2 4 2	1.3517	17.5	69.48	69.68	18.1	82.87	83.08
0 0 4	1.3453	3.9	69.86	70.06	4.0	83.36	83.58
4 1 0	1.3391	0.8	70.23	70.43	0.8	83.83	84.05
4 0 1	1.3187	0.4	71.49	71.69	0.5	85.43	85.66
1 0 4	1.3059	0.3	72.29	72.50	0.3	86.47	86.70
3 3 2	1.2950	0.4	73.00	73.21	0.5	87.38	87.62
2 5 1	1.2934	0.8	73.11	73.32	0.9	87.52	87.75

(Continued)

TABLE 1 (Continued)

		Copper Radiation			Cobalt Radiation		
h k l	d(A)	I	2θ°(α 1)	2θ°(α 2)	I	2θ°(α 1)	2θ°(α 2)
1 5 2	1.2909	0.4	73.27	73.48	0.4	87.72	87.96
2 3 3	1.2909	0.5	73.27	73.48	0.5	87.73	87.96
1 1 4	1.2873	0.4	73.51	73.72	0.5	88.04	88.28
4 2 0	1.2814	0.3	73.91	74.12	0.4	88.55	88.79
3 4 1	1.2777	1.1	74.16	74.37	1.2	88.87	89.12
3 1 3	1.2579	0.6	75.52	75.74	0.7	90.65	90.90
1 2 4	1.2357	0.4	77.12	77.35	0.4	92.75	93.01
4 0 2	1.2138	2.5	78.78	79.01	2.8	94.94	95.21
3 2 3	1.2097	4.6	79.11	79.34	5.3	95.37	95.64
1 6 1	1.2084	5.9	79.20	79.44	6.9	95.50	95.78
2 0 4	1.2059	0.5	79.40	79.64	2.9	95.77	96.05
4 1 2	1.1988	0.6	79.97	80.20	0.7	96.52	96.80
2 5 2	1.1940	0.6	80.35	80.59	0.7	97.03	97.31
2 1 4	1.1911	0.25	80.59	80.83	0.3	97.35	97.63
0 5 3	1.1633	0.24	82.93	83.18	0.3	100.52	100.82
1 3 4	1.1621	0.4	83.04	83.29	0.6	100.66	100.96
3 5 1	1.1420	0.9	84.83	85.09	1.1	103.12	103.43
3 3 3	1.1403	0.9	84.99	85.25	1.2	103.34	103.65
1 5 3	1.1376	0.5	85.24	85.50	0.6	103.69	104.00
4 4 0	1.1080	3.2	88.09	88.36	4.5	107.67	108.01
0 4 4	1.0999	3.2	88.91	89.19	4.4	108.83	109.18
4 3 2	1.0958	1.1	89.33	89.61	1.6	109.44	109.79
0 7 1	1.0699	0.23	92.11	92.40	0.4	113.46	113.84
3 1 4	1.0698	0.27	92.12	92.41	0.4	113.47	113.85
5 0 1	1.0665	0.4	92.48	92.78	0.6	114.01	114.39
5 1 1	1.0563	1.1	93.65	93.95	1.7	115.74	116.14
5 2 1	1.0272	1.7	97.16	97.48	2.9	121.10	121.54
4 4 2	1.0245	3.3	97.50	97.83	5.9	121.64	122.09
3 6 1	1.0232	3.0	97.67	97.99	5.3	121.90	122.35
1 6 3	1.0200	4.3	98.08	98.41	7.8	122.55	123.00
2 4 4	1.0197	3.4	98.12	98.45	6.1	122.62	123.07
1 2 5	1.0176	4.7	98.40	98.73	8.6	123.05	123.51
4 5 0	1.0160	0.6	98.60	98.93	1.1	123.38	123.84
5 3 1	0.9838	1.0	103.07	103.43	2.1	130.81	131.35
4 0 4	0.9565	1.6	107.29	107.68	4.1	138.54	139.19
0 8 0	0.9552	1.2	107.49	107.88	2.9	138.93	139.59
4 1 4	0.9490	0.6	108.52	108.91	1.7	140.97	141.67
5 4 1	0.9312	0.7	111.62	112.04	2.2	147.72	148.58
5 0 3	0.9303	0.6	111.79	112.21	1.9	148.11	148.99
4 2 4	0.9278	0.5	112.24	112.67	1.7	149.20	150.11
1 8 1	0.9268	0.20	112.44	112.87	0.7	149.68	150.61
3 0 5	0.9255	0.16	112.67	113.10	0.5	150.26	151.21
5 1 3	0.9235	0.8	113.05	113.48	2.7	151.22	152.20
3 7 1	0.9215	0.30	113.43	113.86	1.1	152.21	153.23
3 1 5	0.9188	0.4	113.94	114.38	1.4	153.60	154.68
6 0 0	0.9068	0.6	116.32	116.78	3.0	161.15	162.71
5 2 3	0.9039	3.2	116.90	117.37	19.1	163.48	165.28
2 8 0	0.9013	2.8	117.45	117.92	19.9	165.97	168.15
3 6 3	0.9012	3.1	117.47	117.94	22.1	166.07	168.26
0 8 2	0.9002	2.8	117.68	118.15	21.6	167.16	169.58
3 2 5	0.8995	5.2	117.82	118.30	42.8	167.94	170.57
0 0 6	0.8968	0.8	118.39	118.87	9.2	171.76	176.63
4 3 4	0.8954	0.34	118.70	119.18	6.4	174.88	

TABLE 1A

h k l	d(A)	I	Copper Radiation 2θ°(α1)	2θ°(α2)
6 2 0	0.8822	0.20	121.64	122.16
3 5 4	0.8822	0.4	121.64	122.16
2 7 3	0.8821	0.22	121.67	122.18
5 5 1	0.8746	0.9	123.46	123.99
5 3 3	0.8738	0.6	123.65	124.18
6 0 2	0.8593	1.3	127.39	127.97
4 4 4	0.8553	3.3	128.49	129.00
2 8 2	0.8546	4.4	128.68	129.27
6 3 0	0.8542	0.7	128.77	129.37
6 1 2	0.8539	0.9	128.87	129.47
2 0 6	0.8517	1.7	129.48	130.09
6 2 2	0.8383	0.7	133.52	134.19
7 7 4	0.8376	0.31	133.76	134.43
5 4 3	0.8364	1.0	144.13	134.81
3 8 1	0.8349	0.4	134.62	135.31
3 4 5	0.8329	0.23	135.29	135.98
2 2 6	0.8313	0.37	135.82	136.52
3 7 3	0.8293	0.9	136.51	137.23
6 4 0	0.8192	1.6	140.22	141.02
5 6 1	0.8177	2.4	140.80	141.61
6 3 2	0.8142	0.4	142.20	143.05
1 6 5	0.8128	6.5	142.78	143.63
0 4 6	0.8118	2.3	143.19	144.05
4 7 2	0.8117	1.5	143.25	144.11
4 5 4	0.8108	1.3	143.64	144.52
2 7 4	0.8095	0.4	144.28	145.18
6 0 3	0.8092	0.28	144.31	145.21
2 3 6	0.8078	0.26	144.96	145.87
5 3 4	0.8029	0.5	147.24	148.23
2 9 1	0.8015	0.28	147.94	148.94
5 5 3	0.7947	1.6	151.55	152.70
3 5 5	0.7917	1.3	153.32	154.55
6 4 2	0.7836	5.4	158.82	160.40
4 8 0	0.7817	4.4	160.41	162.13
0 8 4	0.7788	5.3	163.01	165.04
2 4 6	0.7799	9.4	163.94	166.11
2 9 2	0.7761	1.0	166.03	168.58
4 4 5	0.7720	0.6	172.42	

TABLE 2

ANALYSIS OF CALCINED PEROVSKITE POWDER

Element	Wt%	Element	Wt%
Ca	28.82	Mo	< 0.004
Ti	26.54	Fd	< 0.004
Al	0.103	Ag	< 0.004
Si	< 0.04	Cd	0.008
Cr	< 0.002	Ba	0.011
Fe	0.044	Ce	< 0.03
Sr	0.013	Nd	< 0.03
Zr	0.533	U	< 0.07

TABLE 3

DATA USED FOR DETERMINATION OF LATTICE PARAMETERS OF PEROVSKITE

h k l	Radiation	2θ(°)	e.s.d.
3 3 1	Co $K\bar{\alpha}$	77.857	0.031
4 0 0	$\bar{\alpha}$	82.304	0.025
4 0 2	α1	94.925	0.029
5 2 1	α1	121.032	0.033
1 6 3	α1	122.520	0.013
2 4 4	α1	122.520	
1 2 5	α1	123.027	0.006
1 2 5	α2	123.590	0.018
5 1 3	α1	151.135	0.061
5 1 3	α2	152.136	0.042
3 7 1	α1	152.136	
6 0 0	α1	160.817	0.056
5 2 3	α1	163.319	0.015
3 6 3	α1	165.952	0.015
2 8 0	α1	165.952	
3 3 1	Cu $K\bar{\alpha}$	65.553	0.024
4 0 0	α	60.000	0.009
4 0 2	α1	78.752	0.015
5 2 1	α1	97.058	0.022
1 6 3	α1	98.046	0.041
2 4 4	α1	98.046	
1 2 5	α1	98.428	0.037
6 0 0	α1	116.186	0.029
5 2 3	α1	116.861	0.016
6 4 0	α1	140.055	0.030
5 6 1	α1	140.793	0.044
5 5 3	α1	151.421	0.045
6 4 2	α1	158.695	0.078
6 4 2	α2	160.346	0.044
4 8 0	α1	160.346	
4 8 0	α2	162.061	0.044
0 8 4	α1	163.030	0.038
2 4 6	α1	163.943	0.041
2 4 6	α2	166.145	0.056

TABLE 4
LATTICE PARAMETERS OF PEROVSKITE, Pnma (A)

Parameter	This Work	A	B	C
a	5.4424 (1)	5.4439 (1)	5.4405 (2)	5.4403 (5)
b	7.6417 (2)	7.6438 (1)	7.6436 (5)	7.6414 (7)
c	5.3807 (1)	5.3670 (1)	5.3812 (3)	5.3810 (5)

A. Kay and Bailey [1957]
B. Swanson *et al.* [1971]
C. Re-analysed data of Swanson *et al.* [1971].

Standard derivations in parentheses are in units of least significant figure of quoted value.

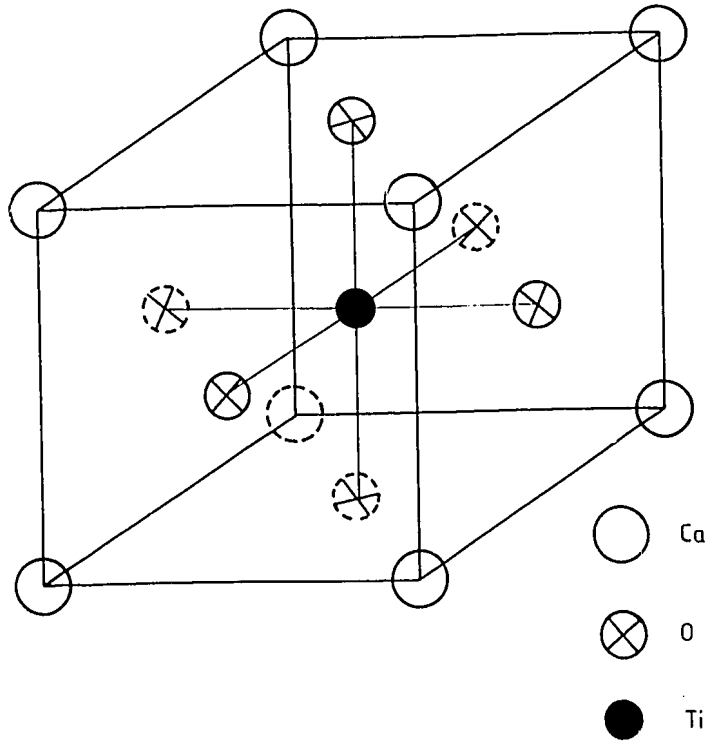
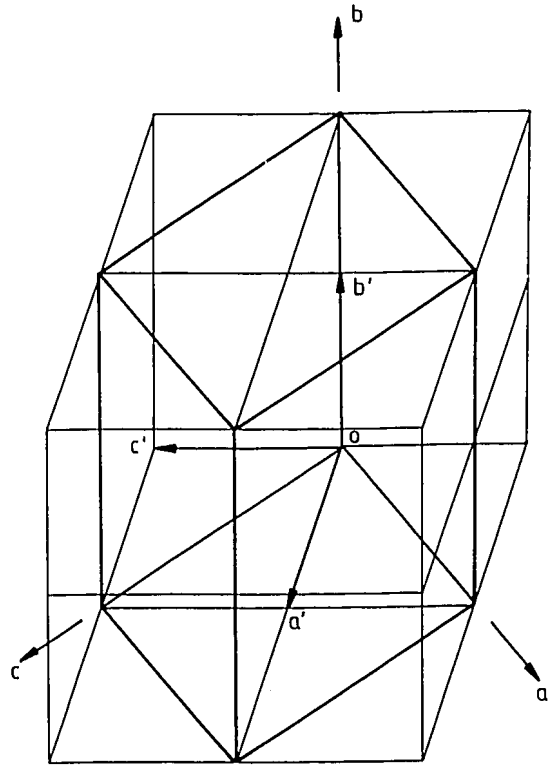


Figure 1 The ideal perovskite structure



a = a'- c'
b = 2b'
c = a'+c'

Figure 2 Relation of perovskite unit cell to pseudo-cubic sub-cell

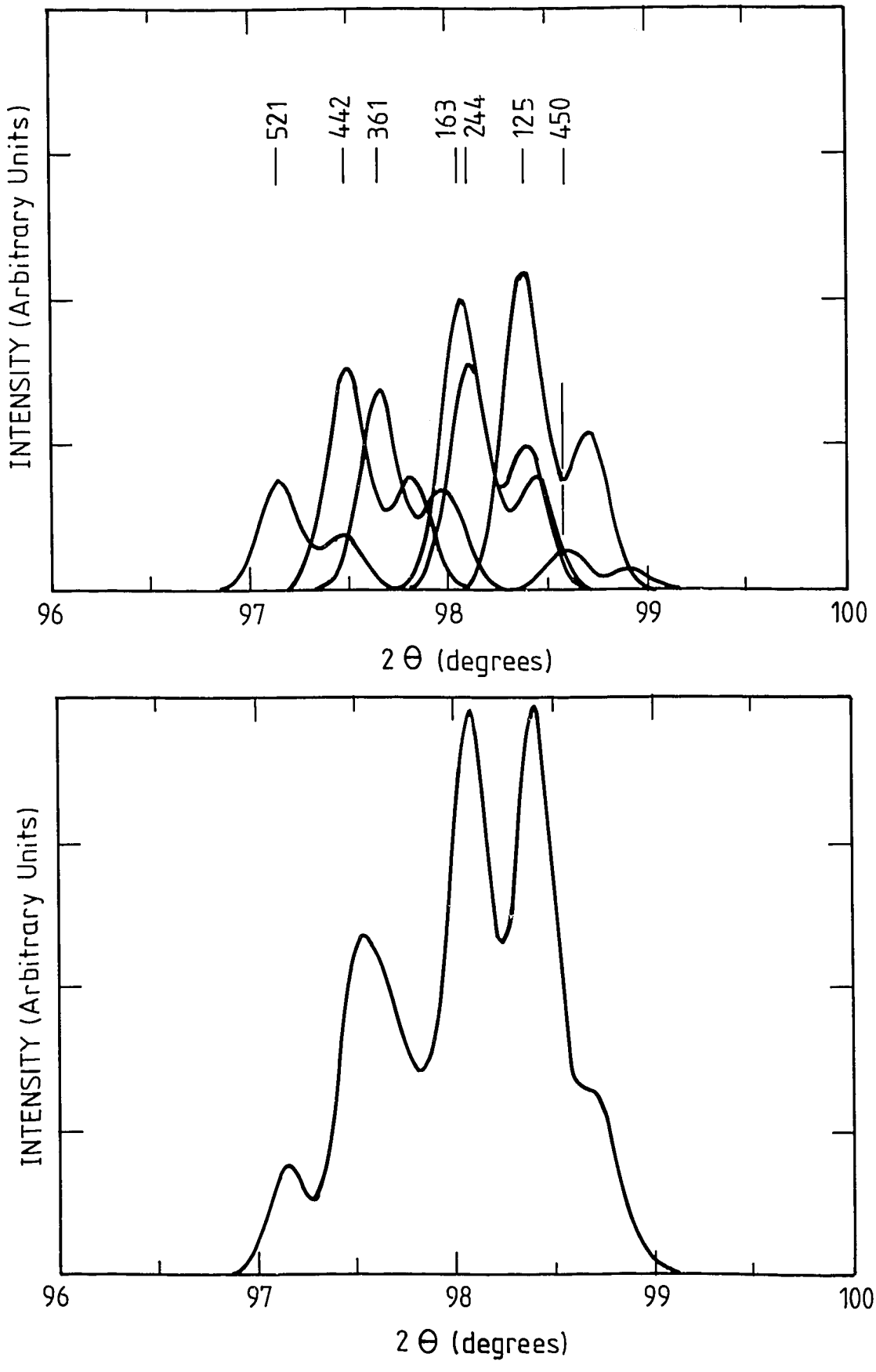


Figure 3 Calculated intensity profile, 521 group, Cu Kα radiation

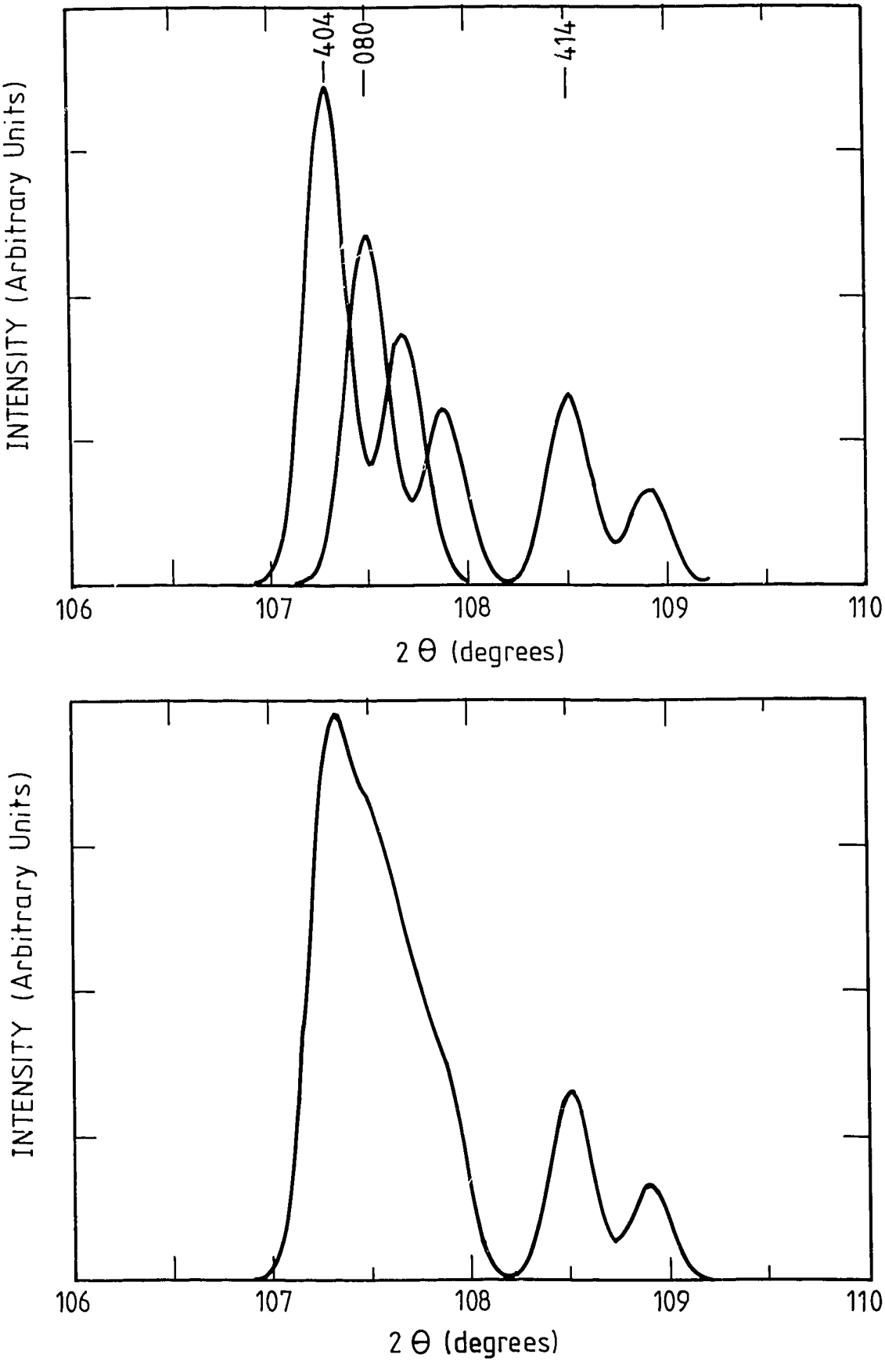


Figure 4 Calculated intensity profile, lines 404 and 080, Cu Kα radiation

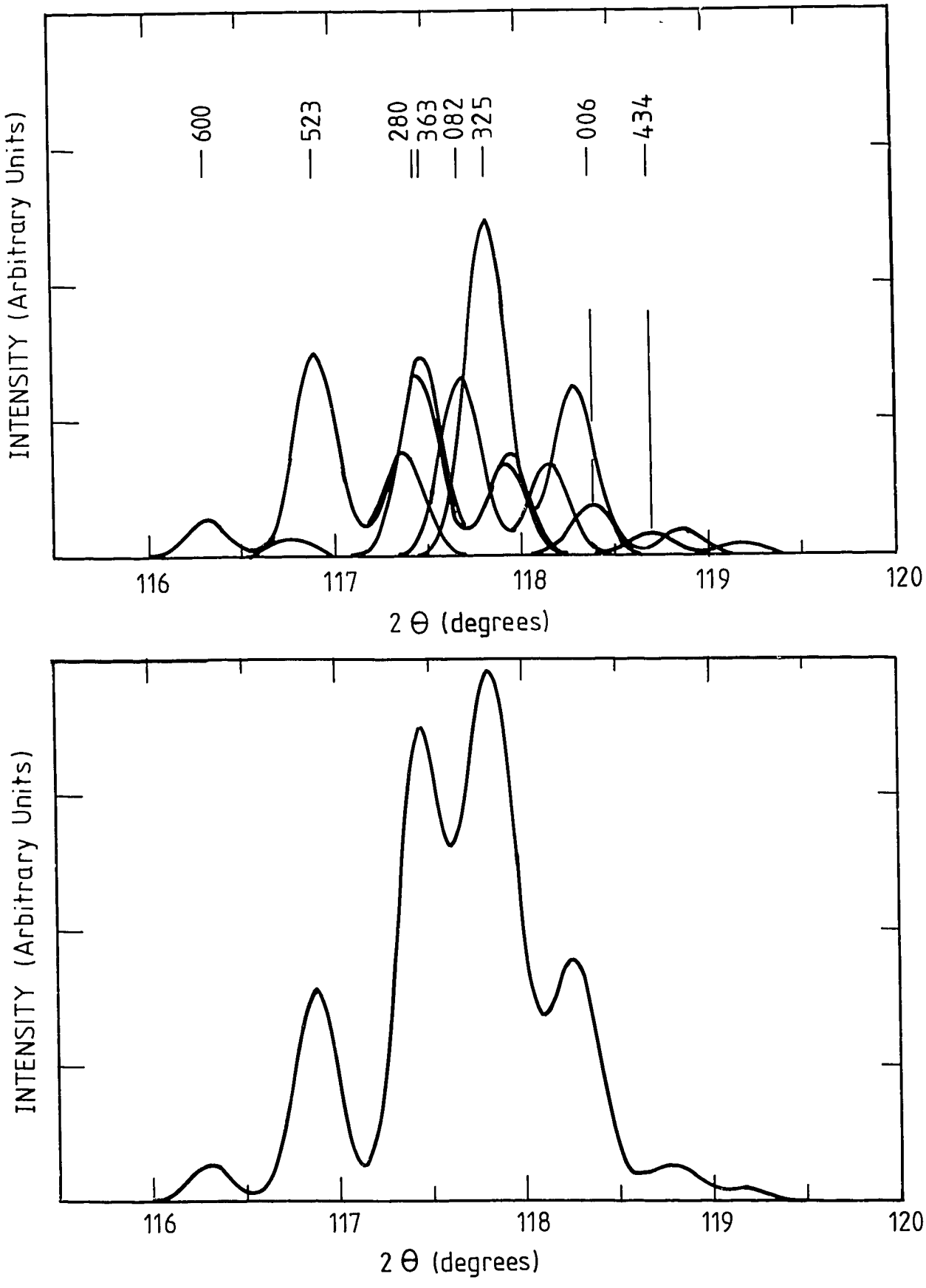
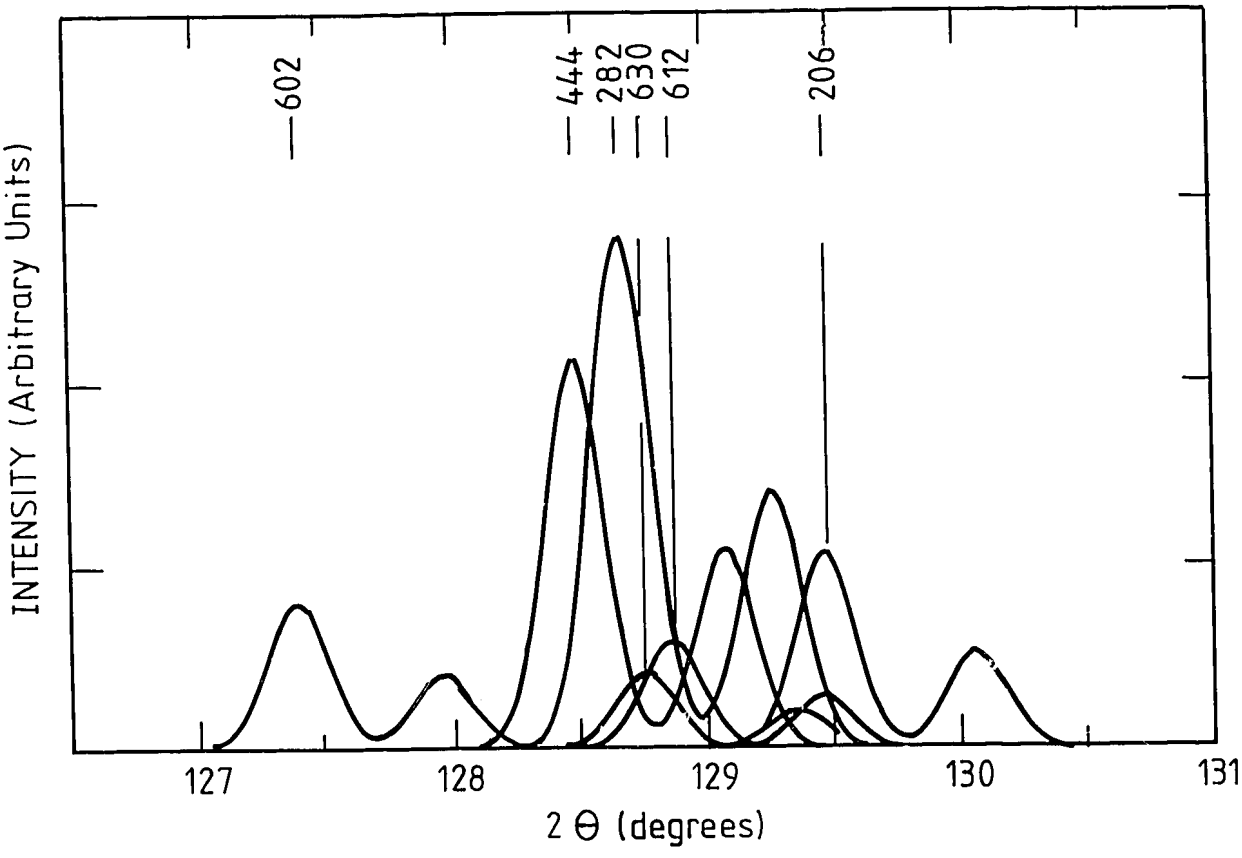


Figure 5 Calculated intensity profile, 600 group, Cu Kα radiation



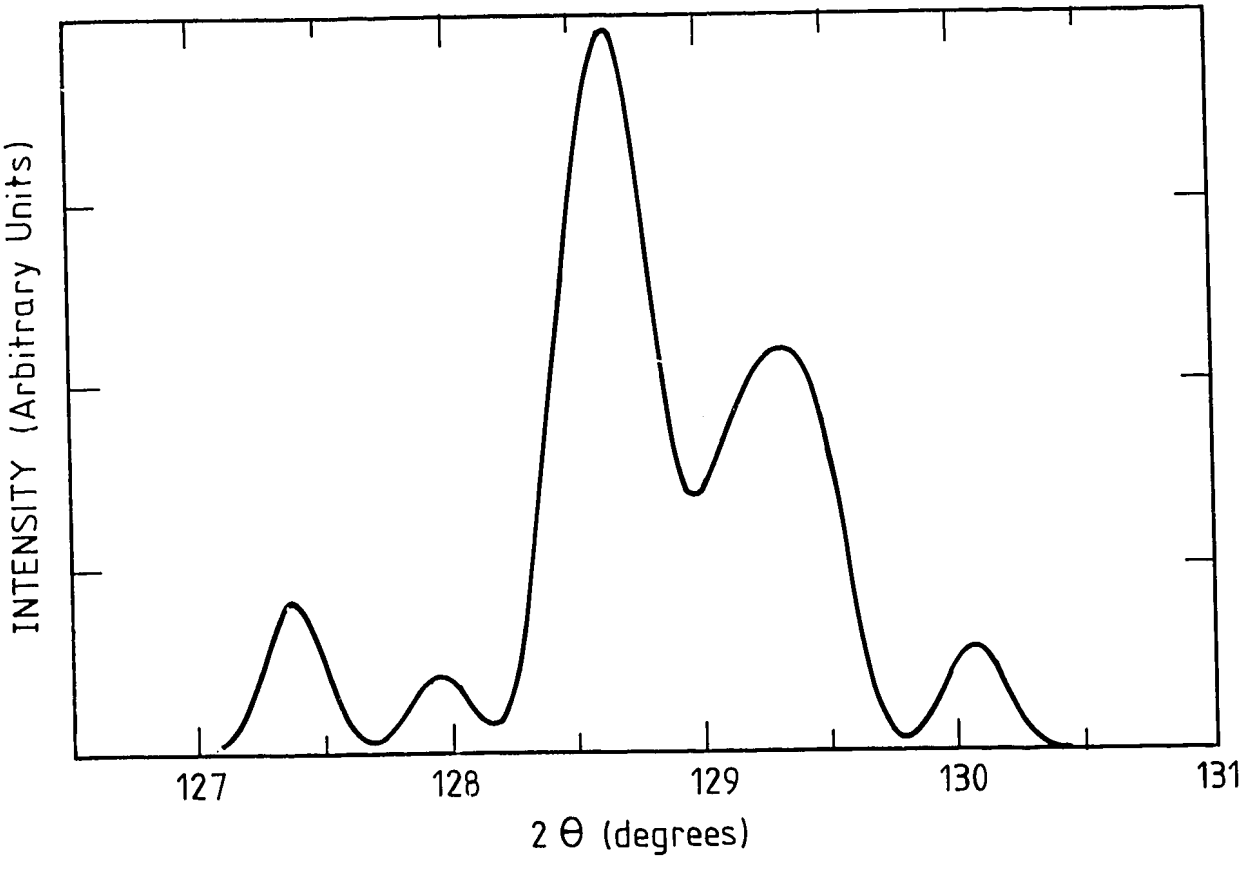


Figure 6 Calculated intensity profile, 602 group, Cu Kα radiation

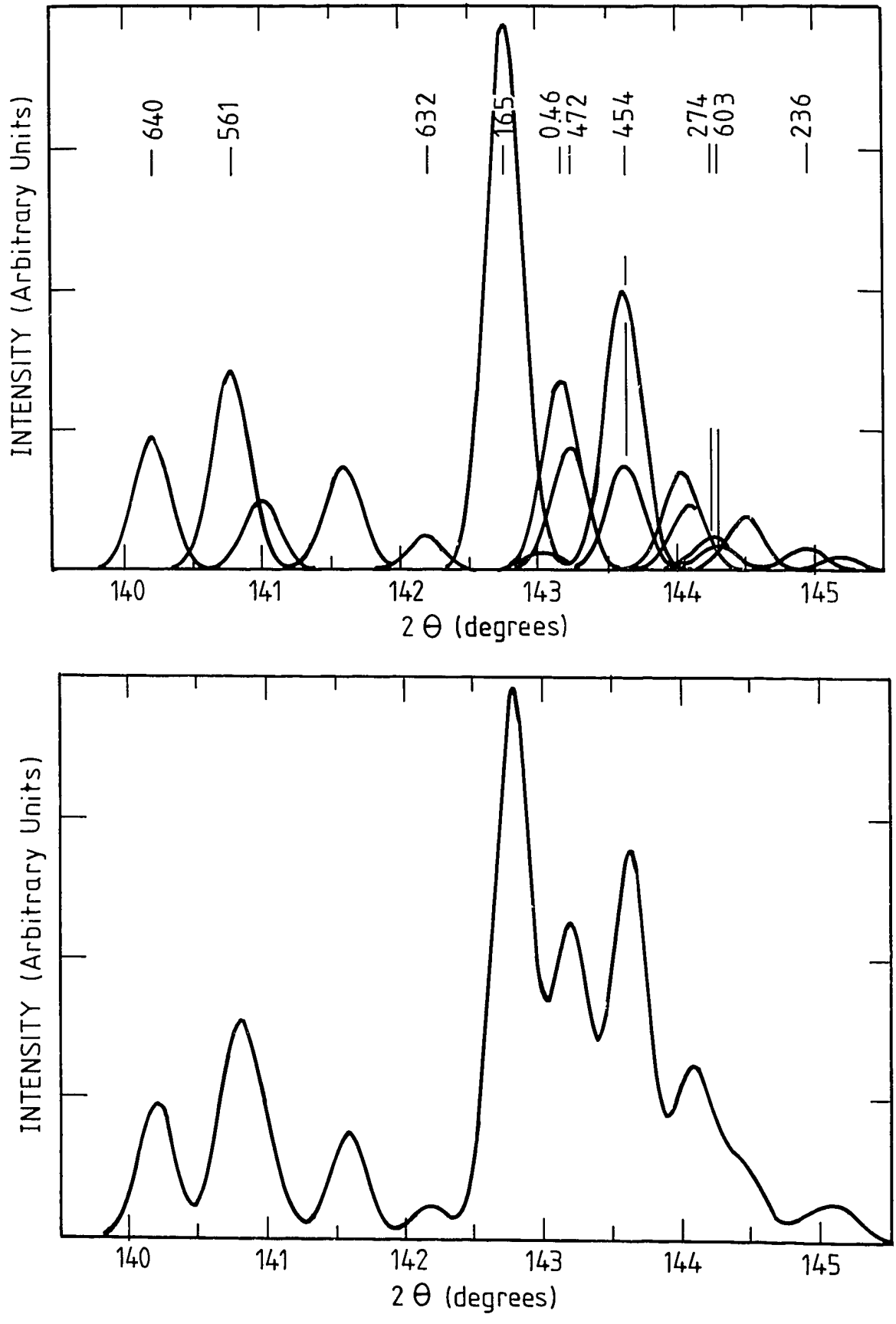


Figure 7 Calculated intensity profile, 640 group, Cu Kα radiation

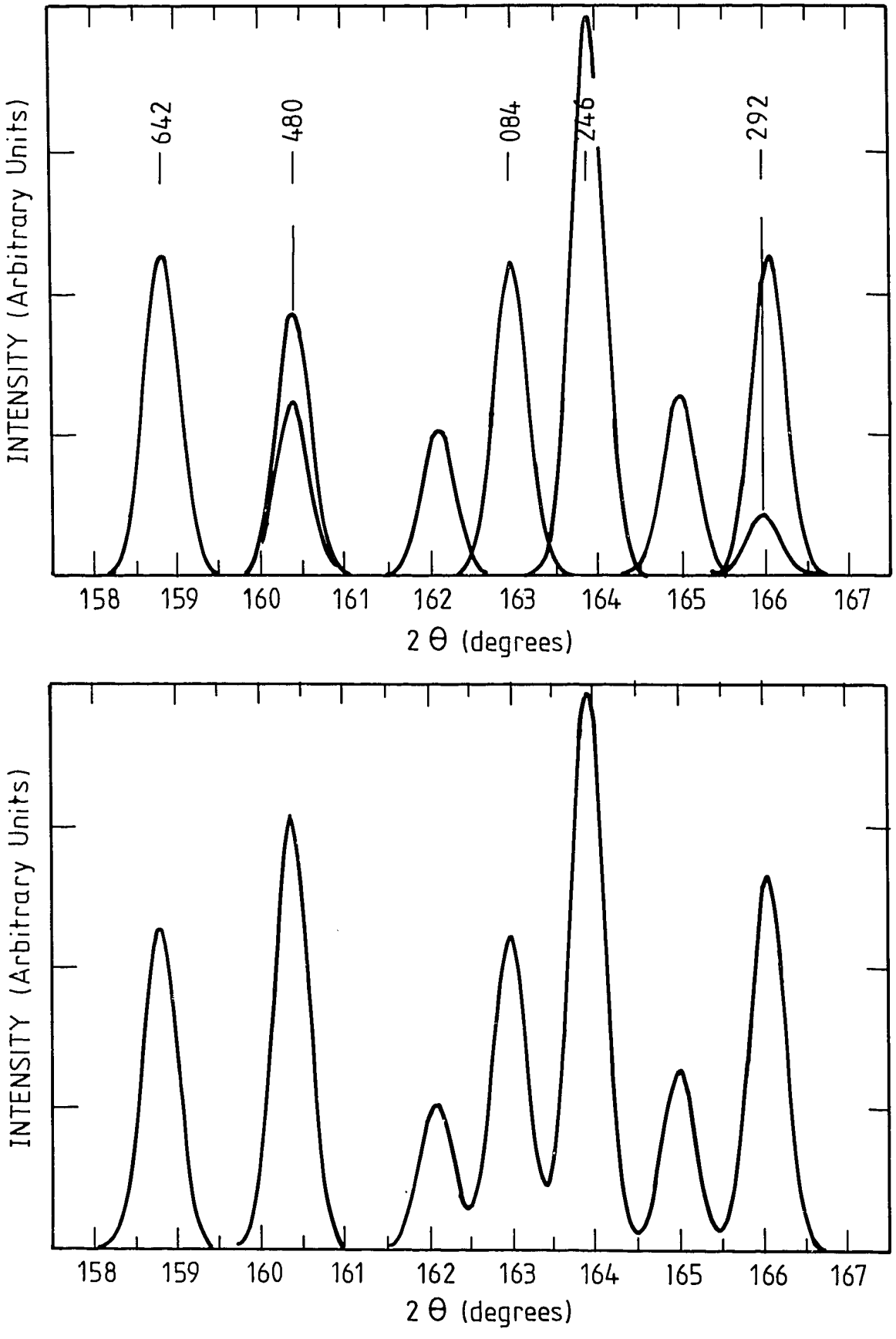


Figure 8 Calculated intensity profile, 642 group, Cu Kα radiation

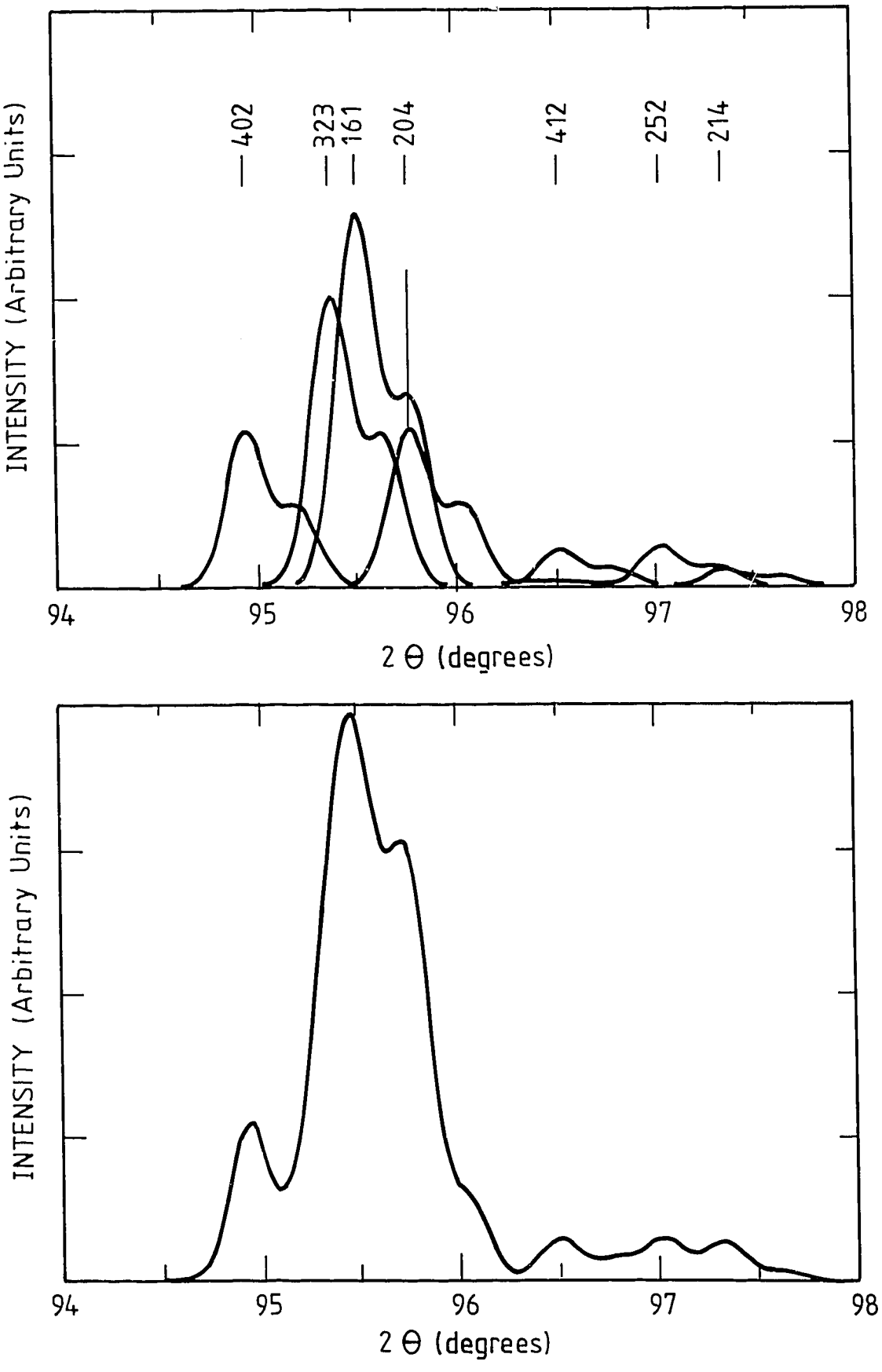


Figure 9 Calculated intensity profile, 402 group, Co Kα radiation

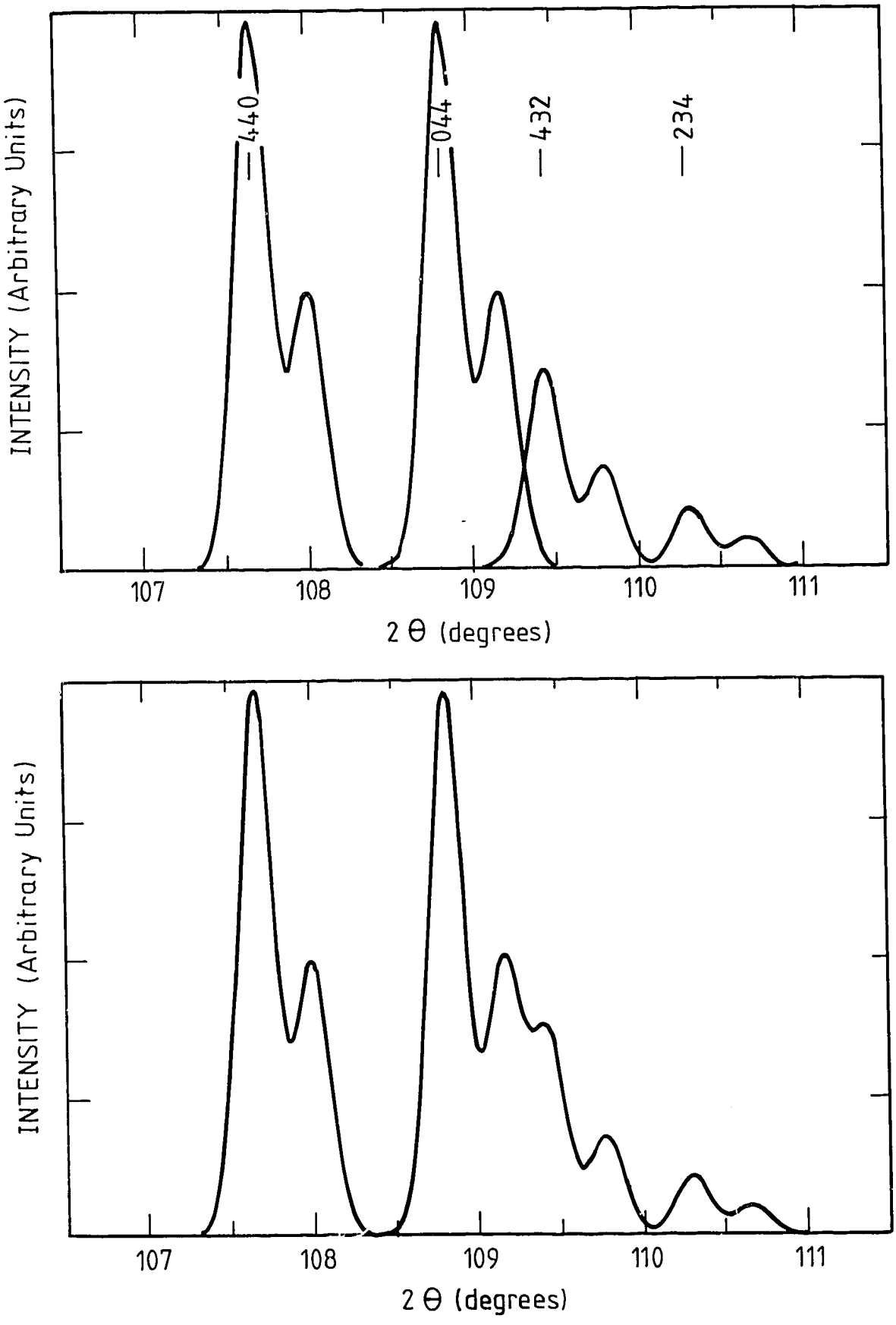


Figure 10 Calculated intensity profile, 440 group, Co Kα radiation

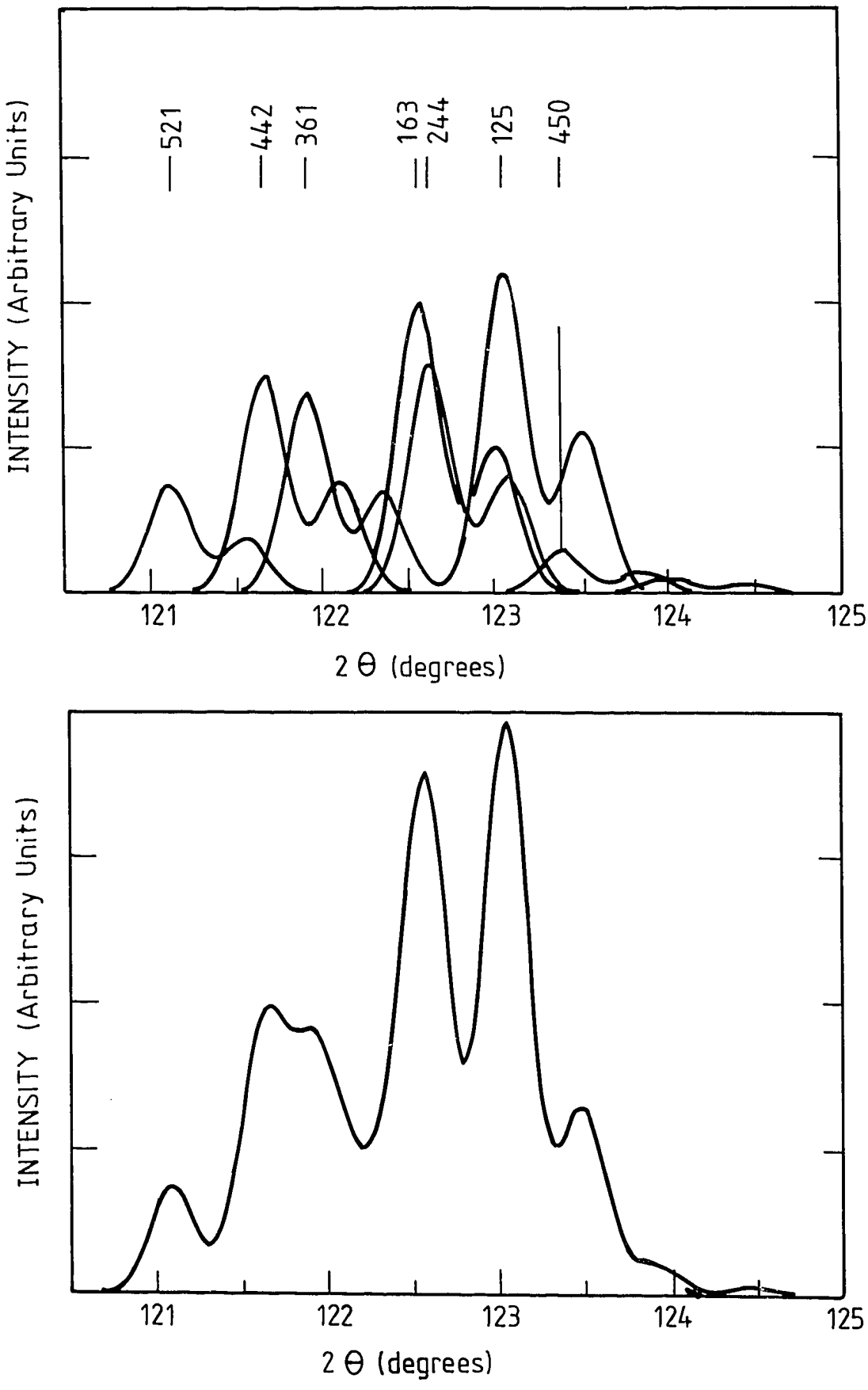


Figure 11 Calculated intensity profile, 521 group, Co Kα radiation

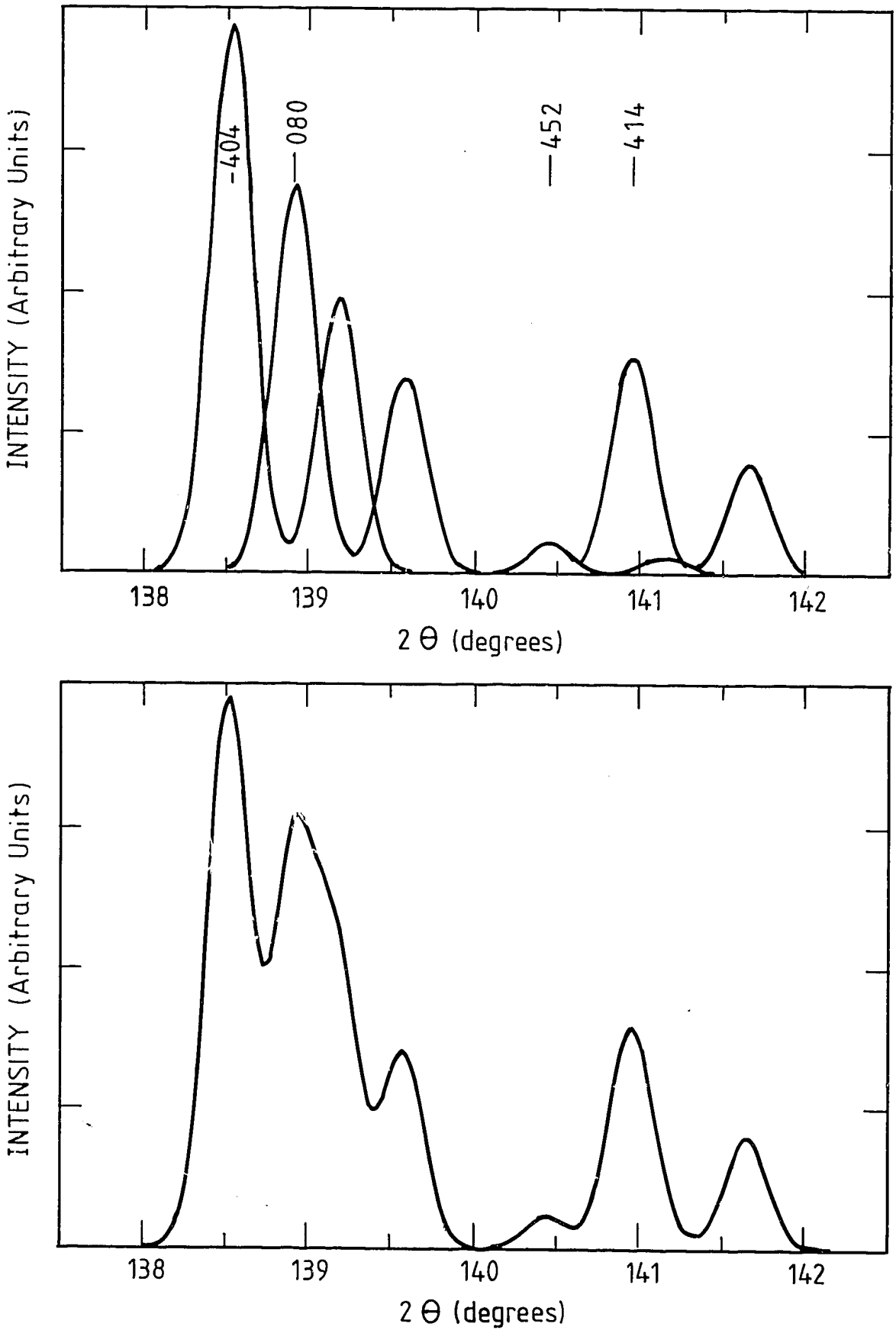


Figure 12 Calculated intensity profile, lines 404 and 080, Co Kα radiation

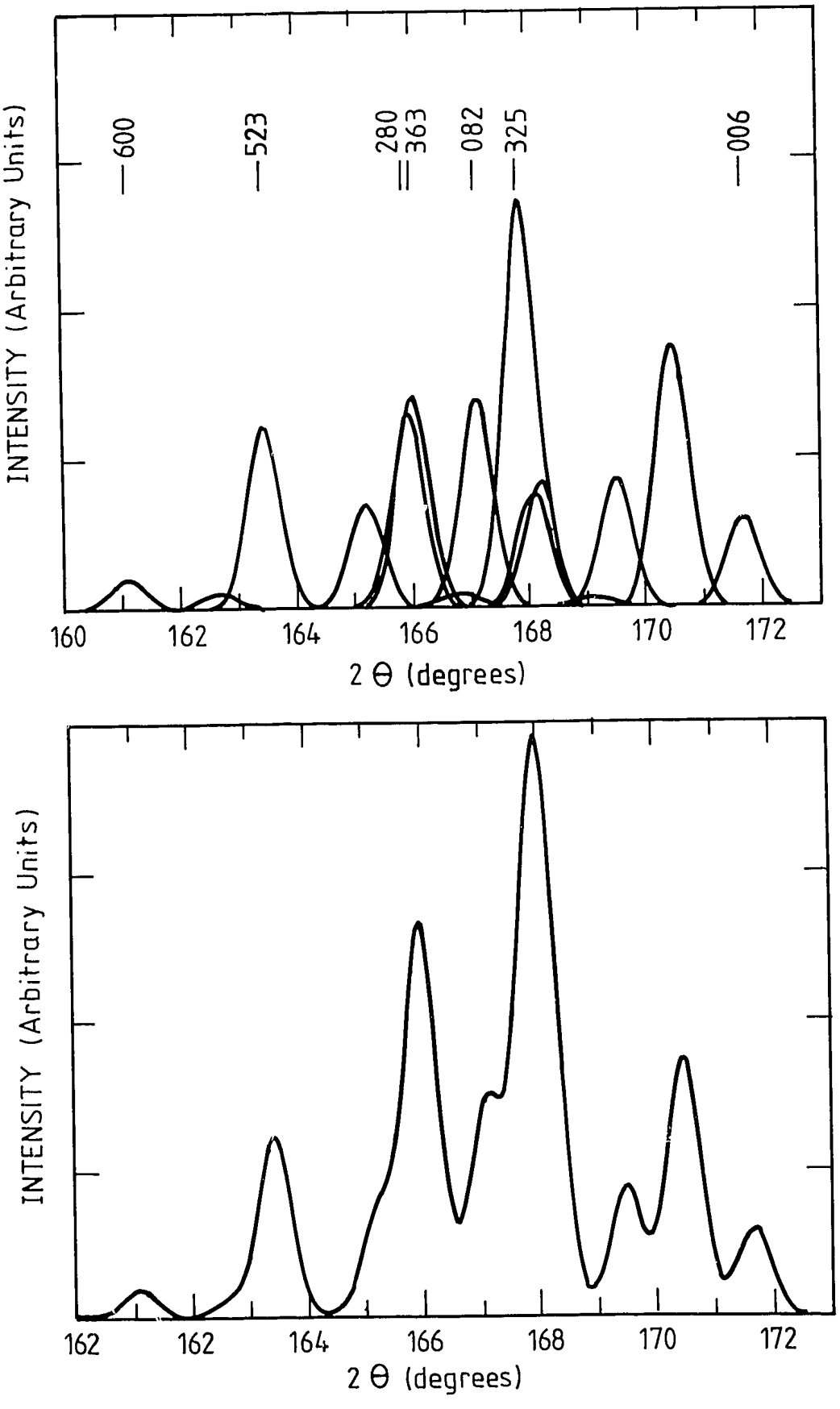
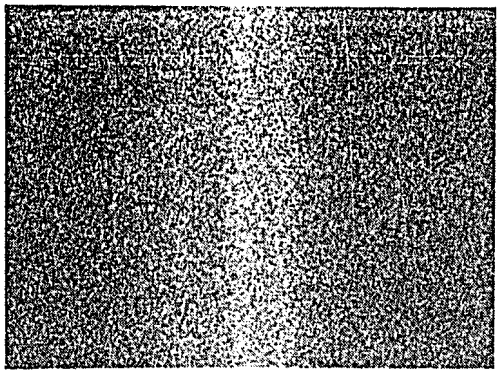
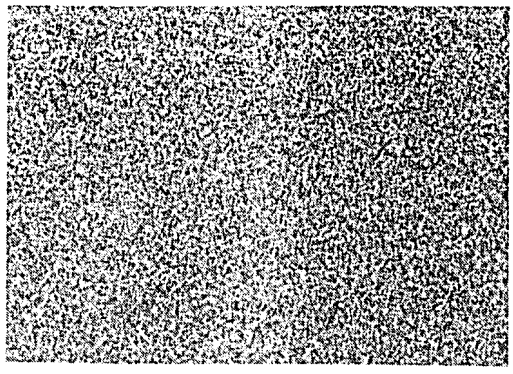


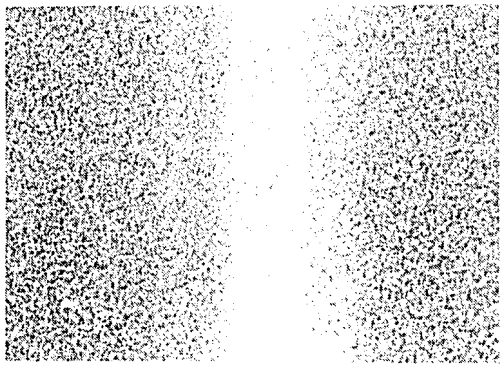
Figure 13 Calculated intensity profile, 600 group, Co Kα radiation



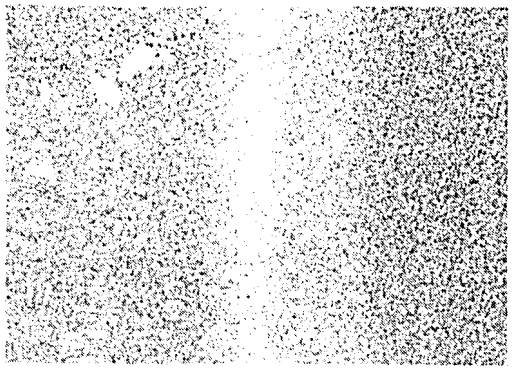
(a) 521 group, *cf* Fig. 3



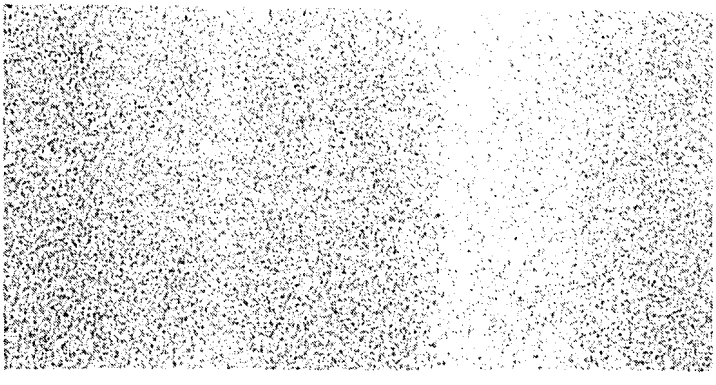
(b) lines 404 and 080, *cf* Fig. 4



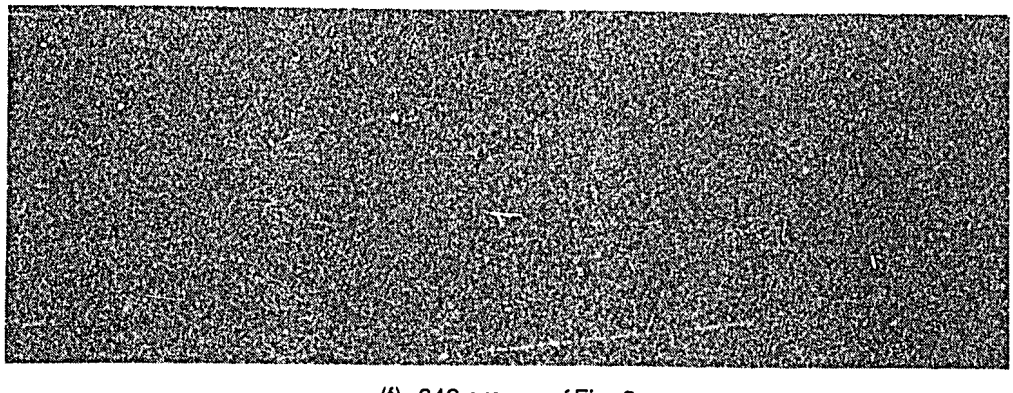
(c) 600 group, *cf* Fig. 5



(d) 602 group, *cf* Fig. 6

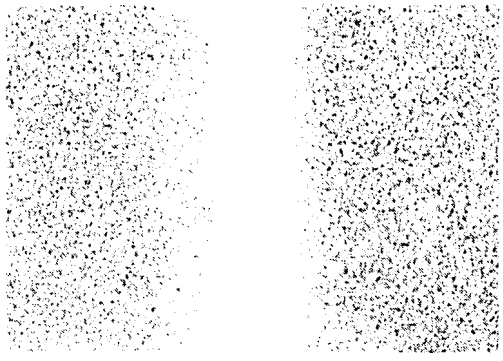


(e) 640 group, *cf* Fig. 7

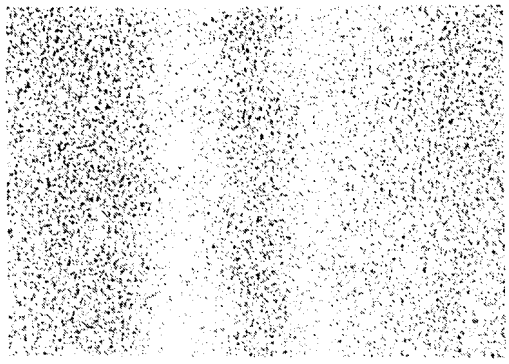


(f) 642 group, *cf* Fig. 8

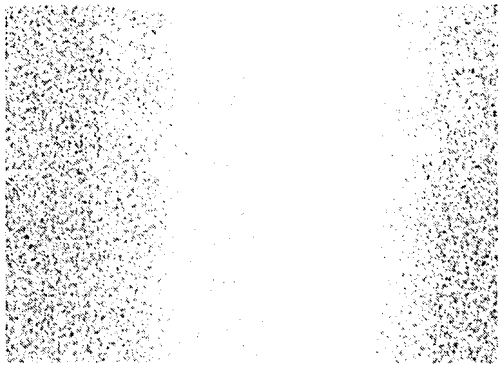
Figure 14 X-ray powder diffraction photographs of perovskite, showing enlargements of various groups of lines, as indicated: Cu radiation



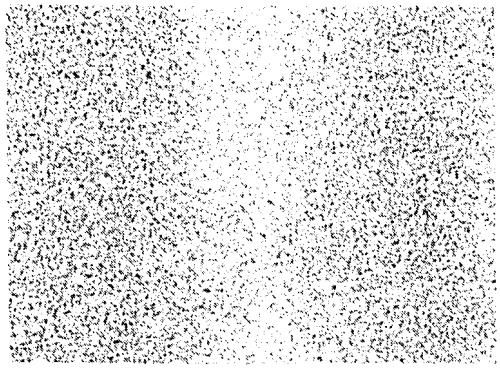
(a) 402 group, *cf* Fig. 9



(b) 440 group, *cf* Fig. 10



(c) 521 group, *cf* Fig. 11



(d) lines 404 and 080, *cf* Fig. 12

(e) 600 group, *cf* Fig. 13

Figure 15 X-ray powder diffraction photographs of perovskite, showing enlargements of various groups of lines, as indicated: Co radiation