

ticated theory of Rezanov & Masharov (1962) is the second-worst fit with the experimental results. Equation (2) should have agreed better with experimental results than equation (1) since the former is valid at high temperature (room temperature) at which the experiment was performed, whereas actually it is the worst fit. The present formula [equation (15)] and that of Valvoda & Syneček [equation (6)] give equally good agreement with the experimental results and hence both of them are satisfactory additivity relations for the Debye temperature of a disordered binary substitutional alloy in terms of those of the component metals.

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Precise Measurement of Lattice Parameters of Pseudocubic Lattices*

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For accurate measurements of lattice parameters of materials where symmetry differs only slightly from cubic, difficulties arise in the determination of single lines belonging to the lattice of lower symmetry because of the overlapping profiles of the pseudocubic lines. In this contribution the profiles of single lines of lower symmetry are approximated by the Cauchy curve and the profiles of the pseudocubic lines are considered as superpositioning of these curves. The resolution of the profiles and the determination of the lattice parameters are performed by means of a computer fitting least-squares program. The conditions for solving the problem are discussed and the method is then applied to a pseudocubic perovskite.

I. Introduction

The true crystal lattice of pseudocubic structures differs only slightly from the cubic one and the particular diffraction lines are grouped together around the 'pseudocubic' positions. The line splitting is, therefore, often very small; and in the precise determination of lattice parameters, one encounters the problem of resolving the positions of the single lines. For example, in perovskite-like solid solutions of $\text{PbTi}_y\text{Zr}_{1-y}\text{O}_3$ for $0.10 < y < 0.40$, the true lattice is rhombohedral ($a_r =$

4.13 \AA), but the deviation of the rhombohedral angle α from 90° is only about $16'$.

In this paper, a method for resolving the overlapping pseudocubic profiles is presented; and the method is applied to precise lattice parameter determinations of $\text{PbTi}_y\text{Zr}_{1-y}\text{O}_3$ for $y = 0.10, 0.20, 0.30$ and 0.38 .

II. Method of resolution of profiles

The procedure for resolving overlapping lines is based on the premise that a single diffraction line can be approximated by a particular analytic function and that the profile of overlapping lines can be expressed by the superposition of these single functions.

Various analytic curves for the approximation of the profile of a single line can be used according to the prob-

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lem to be solved. Often one obtains a good approximation using the Cauchy curve

$$i(x) = \frac{v_1}{1 + 4 \left(\frac{x - v_2}{v_3} \right)^2} \quad (1)$$

where x denotes the independent variable of the profile, which is usually a linear function of the diffraction angle θ ; v_1 is the height of the profile above the background, v_2 is the position of the line, *i.e.* the value of x for which the profile takes its maximal value v_1 ; v_3 is the full width of the profile at one half peak height above background. In those instances where the asymmetry of the profile should be taken into account, one can use two parameters for width, the first for $x < v_2$ and the second for $x > v_2$, similarly as employed for the asymmetry of spectral profiles.

For resolving the profiles, it is necessary that the single line be approximated by the particular analytic function $i_n(x, v_{m,n})$ which includes the parameters $v_{m,n}$ characterizing the features of the line: height, position, width, asymmetry, *etc.* The determination of these parameters for each line is essential for the resolution of the superposed profile. The analytical form of the function $i_n(x, v_{m,n})$ need not be the same for all lines considered.

The criterion for the determination of the parameters $v_{m,n}$ for each line n is the fitting of the analytical curve

$$I(x, v_{m,n}) = \sum_n i_n(x, v_{m,n}) \quad (2)$$

to the experimentally determined values $I_e(x_j)$ of the profile of the overlapping lines. Using the least-squares method, the values of the parameters $v_{m,n}$ are determined when the function

$$S(v_{m,n}) = \sum_j [I(x_j, v_{m,n}) - I_e(x_j)]^2 \quad (3)$$

assumes its minimum value.

The determination of $v_{m,n}$ as independent parameters, is possible only in those cases where the diffraction lines are separated sufficiently. In a real situation, involving pseudocubic lattices, there is usually not enough information in the measured profile for such a determination. Accordingly, relations between the constants, following from the nature of diffraction, must be used so as to reduce the number of degrees of freedom. The explicit form of these relations depends on the conditions of the experiment and on the type of problem to be solved.

III. Computer program for the determination of lattice parameters

For lattice parameter measurements the doublets $K\alpha_{1,2}$ are frequently used. The first simple relations between the parameters $v_{m,n}$ follow from those between the components α_1 and α_2 of the doublet

$$v_{1,\alpha_2}/v_{1,\alpha_1} = M \cdot \mu(\theta) \quad (4a)$$

$$v_{3,\alpha_2}/v_{3,\alpha_1} = W \cdot \omega(\theta) \quad (4b)$$

where v_{1,α_2} , v_{1,α_1} are the heights and v_{3,α_2} , v_{3,α_1} are the widths of the components α_2 , α_1 respectively. The constants M and W are unknown but are the same for all diffraction lines, and the factors $\mu(\theta)$ and $\omega(\theta)$, functions of the Bragg angle θ , can be expressed using the Bragg equation and expressions for the intensities of the lines. For those lines with $\theta \leq 80^\circ$, it is reasonable to approximate $\mu(\theta)$ and $\omega(\theta)$ as each equal to unity.

To decrease further the number of independent variables, the positions of single lines can be expressed by the lattice parameters using the Bragg equation and the relation for lattice spacings appropriate to the structure considered. For this it is necessary to take into account the systematic errors which influence the actual position of the lines. The systematic error in the Bragg angle can be assumed by

$$\Delta\theta = k \cdot \varphi \quad (5)$$

where k denotes the constant of proportionality and $\varphi = \pi/2 - \theta$ is the complement of the Bragg angle. Cernohorsky (1968) showed that equation (5) relates to the Nelson-Riley extrapolation function with an accuracy in lattice parameter of better than $5 \times 10^{-4}\%$. Accordingly, one can write, for the positions of the lines, the relation

$$v_{2,n} = X - Y \cdot \varphi_n \quad (6)$$

where X expresses the value of the variable x corresponding to $\theta = 90^\circ$ and Y denotes the modulus of the scale of x . φ_n , the complement of the true Bragg angle is expressed, *e.g.* for a hexagonal lattice, by the relation

$$\varphi_n = \cos^{-1} \left[\frac{\lambda_n}{2a} \sqrt{\frac{4}{3}(h_n^2 + h_n \cdot k_n + k_n^2) + l_n^2 \cdot (a/c)^2} \right] \quad (7)$$

where a and c are the hexagonal lattice parameters, h_n , k_n , l_n are the hexagonal indices of the diffraction line n , and λ_n is the corresponding wavelength of radiation.

For the precisely aligned diffractometer, the variable $x = 2\theta$, where θ is the measured diffraction angle expressed in degrees. When the systematic errors are negligible ($k = 0$), then $X = 180^\circ$ and $Y = 2$. All parameters $v_{2,n}$ of the positions of the lines are then replaced by the lattice parameters only.

In the case of photographic film measurements, the variable x , measured along the equatorial axis of the film, is proportional to the measured diffraction angle by a constant $2D$, where D is the true diameter of the film (after shrinkage corrections). The systematic errors, mainly absorption errors, usually cannot be neglected. Using equation (5) the constant $Y = 2D(1-k)$. The product $D(1-k)$ is called the 'effective diameter' of the camera (Cernohorsky, 1961). For the determination of X and Y , the symmetry of the back reflection lines with respect to the primary beam can be

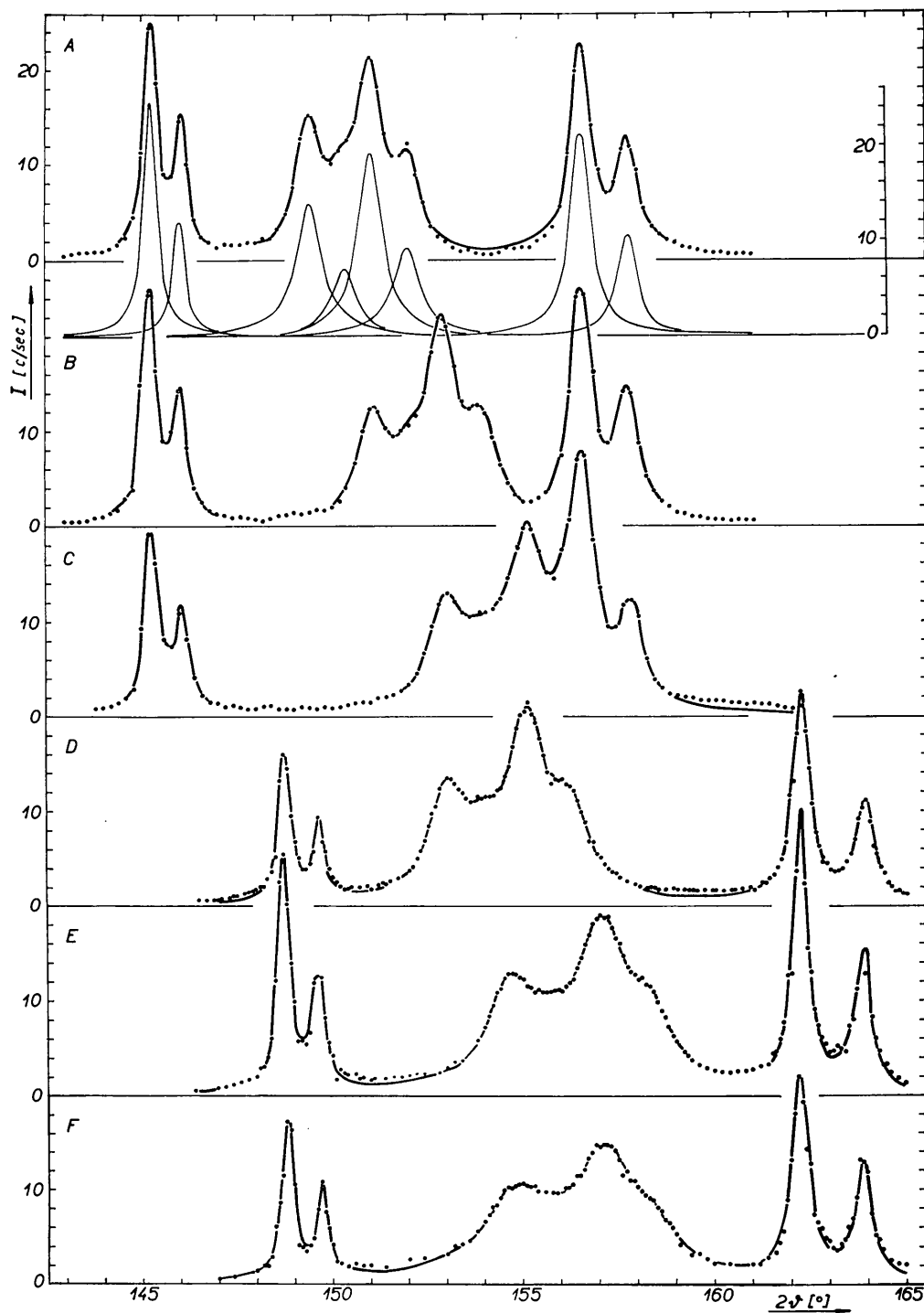


Fig. 1. The results of the fitting procedure for $\text{PbTi}_{1-y}\text{Zr}_{1-y}\text{O}_3$. The dots express the experimental values I_e of profiles after background subtraction. The solid lines represent the resulting calculated profile (omitted when it coincides with a high density of experimental points). In Fig. 1A the resulting profiles of single lines are added on a shifted scale.

- | | |
|---|---|
| A | (I) $\text{PbTi}_{0.10}\text{Zr}_{0.90}\text{O}_3 + \text{Ag}$ |
| B | (I) $\text{PbTi}_{0.20}\text{Zr}_{0.80}\text{O}_3 + \text{Ag}$ |
| C | (I) $\text{PbTi}_{0.30}\text{Zr}_{0.70}\text{O}_3 + \text{Ag}$ |
| D | (I) $\text{PbTi}_{0.30}\text{Zr}_{0.70}\text{O}_3 + \text{Al}$ |
| E | (I) $\text{PbTi}_{0.38}\text{Zr}_{0.62}\text{O}_3 + \text{Al}$ |
| F | (II) $\text{PbTi}_{0.38}\text{Zr}_{0.62}\text{O}_3 + \text{Al}$ |

used or the introduction of external reference lines is necessary. Both X and Y are then determined, together with the lattice parameters and other parameters $v_{m,n}$, by minimizing S in relation (3).

The introduction of reference lines is useful, not only for the determination of X and Y in relation (6), where the known position of the lines is utilized, but also for the determination of the ratio of the heights of doublets [equation (4a)] when the separation of pseudocubic lines is small in relation to their widths. The evaluation of the reference lines is performed in the same way as mentioned above for the pseudocubic lattices, where the angle φ_n is calculated using the appropriate expression for the reference lattice.

The program (FORTRAN IV) based on the foregoing is useful for both diffractometric and film measurements. For approximating the profiles of the diffraction lines, the symmetric Cauchy curve [equation (1)] has been used, but any other function may be substituted by replacing only one arithmetic instruction. The capacity of the program enables one to evaluate a maximum of five reference cubic lines and eight pseudocubic groups of lines with as many as eight single lines in one group. In the present version of the program, the parameters of hexagonal or tetragonal pseudocubic lattices can be evaluated.

The minimization of the sum of the squares of deviations [relation (3)] is performed using a fitting, least-square program (Hnilicka & Karmazin, 1969). Initially the estimated values of the parameters are inserted into the program which calculates the value of S , and by a trial iterative procedure changes the parameters to minimize the value of S . The program performs the minimization of S employing preliminary selected parameters while others are kept constant. This allows appreciable variations of the program with respect to the different relations between the characteristics of the lines, and permits the selection of the system of independent parameters from the input data. The reference lines can be, but need not be, used for the evaluation according to the conditions of experiment.

IV. Measurement of lattice parameters of rhombohedral $\text{PbTi}_y\text{Zr}_{1-y}\text{O}_3$

The foregoing procedure for determining lattice parameters from overlapped profiles was used for the diffractometric measurements of four samples of rhombohedral $\text{PbTi}_y\text{Zr}_{1-y}\text{O}_3$ with $y=0.10, 0.20, 0.30$ and 0.38 . The hexagonal indices 226 and 422, and two reference $\text{Co } K\alpha$ doublets 331 and 420 of either silver or aluminum, were used for the evaluation.

The single lines were approximated by symmetrical Cauchy curves [equation (1)]. For eight lines of four doublets, a total of 24 parameters had to be determined. To decrease the number of independent parameters, the relations (4a) and (4b) were used. In equation (4a) M was determined with $\mu(\theta)=1$. In equation (4b) both $\omega(\theta)$ and W were set equal to unity.

The positions of the lines were expressed by equation (6) where the angles φ_n were determined from equation (7) for $\text{PbTi}_y\text{Zr}_{1-y}\text{O}_3$. A similar relation

$$\varphi_n = \cos^{-1} \left[\frac{\lambda_n}{2A} \sqrt{h_n^2 + k_n^2 + l_n^2} \right] \quad (8)$$

was used for the reference lines, where h_n, k_n, l_n are the cubic indices and A is the lattice parameter of the reference material. The determination of intensity profiles of the lines was performed on a goniometer where, in principle, the constants X and Y of equation (6) can be determined by independent measurements. However, the values of X and Y were determined on the basis of the known positions of the reference lines so as to avoid the independent alignment of the zero point of the goniometer. Moreover it was possible to eliminate the small, residual eccentricity of the sample mounting from a determination of Y . The evaluation in this respect was carried out as for photometric film measurements.

By use of the foregoing procedure, the 24 parameters were reduced to 12 independent ones: two hexagonal lattice parameters, two heights, one common width of the doublets of $\text{PbTi}_y\text{Zr}_{1-y}\text{O}_3$, two heights and two widths of the reference doublets, one common ratio of the intensities of the α_1 and α_2 components of the doublets, and two parameters X and Y .

The measurement of the experimental profiles was performed at 25°C on a G.E. XRD-5 diffractometer using $\text{Co } K\alpha$ radiation. Sintered, solid samples of $\text{PbTi}_y\text{Zr}_{1-y}\text{O}_3$ were used, the surfaces of which were carefully polished. The reference material, silver or aluminum both of purity 99.999%, in the form of heat-treated filings (particle size $< 43 \mu\text{m}$) was placed on the surface of the samples by means of a thin layer of vaseline. The lattice parameters of the reference material were determined using a Straumanis asymmetric camera. Results of 4.0862 \AA for silver and 4.0496 \AA for aluminum, both at 25°C , are in agreement with the reported values of Pearson (1967).

V. Results and conclusions

The experimental results of the profiles, after subtraction of background, are shown dotted in Fig. 1. The solid lines drawn through the experimental points are the resulting superposed analytical curves as determined by the computer technique. In Fig. 1A the resulting profiles of single lines are added for illustration.

Table 1. Results of parameter measurements of $\text{PbTi}_y\text{Zr}_{1-y}\text{O}_3$

y	Samples	a (Å)	c/a	a_r (Å)	$90^\circ - \alpha$ (°)	w (°)
0.10	I + Ag	5.8414	1.23344	4.1403	16.26	0.76
0.20	I + Ag	5.8174	1.23385	4.1237	17.03	0.87
0.30	I + Ag	5.7917	1.23463	4.1064	18.48	1.16
0.30	I + Al	5.7918	1.23464	4.1065	18.49	1.13
0.38	I + Al	5.7705	1.23537	4.0922	19.85	1.47
0.38	II + Al	5.7706	1.23541	4.0923	19.93	1.73

The lattice parameters and widths of $\text{PbTi}_y\text{Zr}_{1-y}\text{O}_3$ are given in Table 1 where a_r and α denote the transformed rhombohedral lattice parameters.

In addition to the basic series of samples, denoted as (I) (Table 1, Fig. 1), three more measurements were made for estimating the precision. Two are given in Table 1. For $y=0.30$ the same sample was used as in the basic series, but the reference material was silver rather than aluminum. For $y=0.38$ another sample of the same composition was used employing a different technique for polishing the sample surface. A third measurement was made to compare the reference materials. Here silver was used as the reference material and the lattice parameter of aluminum was determined as for the pseudocubic samples. The measured value of

aluminum was 4.0496_4 \AA at 25°C in agreement with the reported value of 4.0496 \AA .

On the basis of these results, it is concluded that the precision of the determination of the lattice parameters of $\text{PbTi}_y\text{Zr}_{1-y}\text{O}_3$ in this study is of the order of 0.005%.

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Electron Microscope Study of an Homologous Series of Shear Structures based on Molybdenum Trioxide

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Electron microscopy and diffraction evidence is presented for the existence of four new molybdenum oxides $\text{Mo}_n\text{O}_{3n-2}$, $n=19, 20, 21$, and 22 .

Introduction

The structural chemistry of the higher molybdenum oxides MoO_x , $2.00 \leq x \leq 3.00$, was thoroughly studied by Magnéli and Kihlberg. They determined and/or refined the crystal structures of MoO_2 , Mo_4O_{11} (monoclinic), Mo_4O_{11} (orthorhombic), $\text{Mo}_{17}\text{O}_{47}$, Mo_5O_{14} , Mo_8O_{23} , Mo_9O_{26} (monoclinic), $\text{Mo}_{18}\text{O}_{52}$ (triclinic), and MoO_3 (see review by Kihlberg, 1963*a*). Magnéli (1953) introduced the idea of homologous series to describe the structural relationship between Mo_8O_{23} , Mo_9O_{26} and an hypothetical MoO_3 with ReO_3 -type structure. He proposed a method for deducing the unit cell and atomic positions for unknown members of the series. Further members were then found in the mixed oxides $(\text{Mo}, \text{W})_n\text{O}_{3n-1}$ with $n=10, 11, 12$, and 14 . There was almost complete agreement between the observed and predicted structures.

It has remained puzzling that Magnéli phases with $n \geq 10$ did not appear in the pure molybdenum oxides. Instead Mo_9O_{26} and MoO_3 appeared to be the only stable phases between 750°C and the melting point 790°C . A completely different structure, $\text{Mo}_{18}\text{O}_{52}$, coexisted with MoO_3 at lower temperatures. Single-crystal studies showed it to be derived from MoO_3 rather than ReO_3 (Kihlberg, 1963*b*). Kihlberg proposed that this was the first member of a new homologous series $\text{Mo}_n\text{O}_{3n-m+1}(\text{MoO}_3)$ with $n=18, m=3$, and $x=$

2.8889. His X-ray patterns suggested that at least four other phases existed but were rare, could not be prepared reproducibly, and were presumed metastable. Approximate unit-cell parameters were derived for two of these and a comparison with the ideal values suggested that they may be $\text{Mo}_{13}\text{O}_{38}$ ($n=13, m=2, x=2.9231$) and $\text{Mo}_{26}\text{O}_{75}$ ($n=26, m=4, x=2.8864$).

Later X-ray studies have revealed a large number of ReO_3 based homologous series (the block structures) in the niobium oxides and oxyfluorides MX_x , $2.4 \leq x \leq 2.7$ (Wadsley & Andersson, 1970). The term crystallographic shear (CS) structures was introduced to describe the formal relation between the members of such series and the parent structures (Wadsley, 1955).

Electron optical studies of TiO_x (Bursill, Hyde, Terasaki & Watanabe, 1969; Bursill & Hyde, 1971) and of $(\text{Ti}, \text{Cr})\text{O}_x$ (Bursill, Hyde & Philp, 1971) in the composition range $1.89 \leq x \leq 1.98$ have revealed numerous homologous series $\text{Ti}_n\text{O}_{2n-a}$ ($1 \leq a \leq 30$) derived from rutile by CS. The X-ray studies (Andersson & Jahnberg, 1963) suggested that the one known series $4 \leq n \leq 9$ merely extended to higher n values. On the contrary new structural principles emerged giving a continuous series of ordered phases reminiscent of the proliferation of phases around Nb_2O_5 . These new phases could not be detected by X-ray diffraction due to their special reciprocal lattice geometry.

We therefore chose to study MoO_x , $2.89 \leq x \leq 3.00$,