Similarly in the phase V → phase IV transformation the anions at F could have aligned themselves on the $(\bar{2}20)_V$ planes rather than the $(220)_V$ planes. The result would then be a structure for phase IV in which the c axis being the same as before, the a and b axes are interchanged. It is possible that with nucleation of the transformation in different parts of the crystal, both kinds of phase IV domains are present at the end of the transformation. The two domains would be related by an element of non-crystallographic symmetry parallel to $A'C'$ in Fig. 1.

Conclusion

An attempt has been made to consider the sequence of transformations, V → IV → II, in ammonium nitrate crystals on the basis of the ideas of martensitic transformations in metals. A similar attempt on the thermal cycle of phase transformations in potassium nitrate was recently published. In particular the aim here was to show that on a least-motion hypothesis (*i.e.* the shuffles are least-motion processes consistent with symmetry and accepted interatomic distances) the higher-symmetry phase structure may be predictable solely from its unit-cell dimensions and space-group symmetry if the low-symmetry phase of the transformation has a completely determined crystal structure. These considerations yield an adequate explanation of twinning observed in the transitions. The ions are treated here as rigid groups. It would be interesting indeed if a structure with high pseudo-symmetry is solved and

the structure of the result of a possible phase transformation were predicted and later succesfully verified.

References

AMOROS, J. L., ARRESE, C. & CANUT, M. (1962). *Z. Kristallogr.* **117**, 92–107.
BAUR, W. H. (1972). *Acta Cryst.* B**28**, 1456–1465.
BROWN, R. N. & McLAREN, A. C. (1962). *Proc. Roy. Soc.* A**266**, 329–343.
CHOI, G. S., MAPES, J. E. & PRINCE, E. (1972). *Acta Cryst.* B**28**, 1357–1361.
CHRISTIAN, J. W. (1965). *The Theory of Phase Transformations in Metals and Alloys.* Oxford: Pergamon Press.
CLEAVER, B., RHODES, E. & UBBELOHDE, A. R. (1963). *Proc. Roy. Soc.* A**276**, 453–460.
HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids.* New York: W. A. Benjamin.
HENDRICKS, S. B., POSNJAK, E. & KRACEK, F. C. (1932). *J. Amer. Chem. Soc.* **54**, 2766–2786.
KITAIGORODSKY, A. I. (1955). *Organischeskaya Kristalloximiya.* U.S.S.R: Izdatelstvo Akademii Nauk.
PAULING, L. (1960). *Nature of the Chemical Bond.* Ithaca: Cornell University Press.
SWAMINATHAN, S. & SRINIVASAN, S. (1975). *Acta Cryst.* A**31**, 628–634.
UBBELOHDE, A. R. (1965). *Melting and Crystal Structures.* Oxford Univ. Press.
WAYMAN, C. N. (1964). *Introduction to the Crystallography of Martensitic Transformations.* New York: Macmillan.

The Squared Power Method to Fit a Plane to a Set of Points*

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The 'power method' provides a computationally easy method for the determination of the best plane through a set of points. By repeatedly taking squares, one rapidly obtains the maximum eigenvalue and corresponding eigenvector of the inertia tensor. The result is the least-squares result when the points have independent, isotropic weights.

Introduction

We present a simple alternative to the use of least-squares techniques (Scheringer, 1971) for the determination of the best plane through a set of points. Though the basic method presented is old (National

Physical Laboratory, 1957) (NPL) and the power method has been discovered by crystallographers more than once (Schomaker, Waser, Marsh & Bergman, 1959), its advantages seem not to have been fully exploited to date. This may well be due to some problems which arise from the particular formulations of the technique chosen in the past. In particular, the method can be subject to slow convergence and capture by the wrong eigenvector. When applied in other eigenvalue searches where negative eigenvalues arise, it can suffer

from oscillation. Following NPL, we overcome these problems simply by repeated squaring, rather than forming successive powers, of the inertia tensor.

Method

Obtaining largest eigenvectors

Consider a matrix A. Assume for the moment it is real and symmetric. Take the series $A, A^2, A^4, A^8, \ldots,$ $A^{2N}, \ldots,$ each the square of the preceding term. Then we can demonstrate that the series rapidly approaches a matrix in which only the eigenvector(s) of the largest eigenvalue appears. For computational convenience, the series can be renormalized at each step. This avoids underflow or overflow.

For proof, one need only recall that A can be looked at as acting on the space with its eigenvectors as basis vectors; *i.e.* with basis vectors $e_1, \ldots, e_n$ such that $Ae_i = \lambda_i e_i$. If σ is the orthogonal matrix which transforms to this new basis, then

$$A = \sigma A' \sigma^{-1}$$

where A' is diagonal with the eigenvalues as the diagonal elements. Then, since

$$A^2 = \sigma A' \sigma^{-1} \sigma A' \sigma$$
$$= \sigma (A')^2 \sigma^{-1},$$

we have

$$A^{2N} = \sigma (A')^{2N} \sigma^{-1}.$$

Now $(A')^{2N}$ is

$$\begin{pmatrix} \lambda_1^{2N} & 0 & 0 & \cdots \\ 0 & \lambda_2^{2N} & 0 & \cdots \\ 0 & 0 & \lambda_3^{2N} & \\ & & & \cdot \\ & & & & \cdot \\ & & & & & \cdot \end{pmatrix}$$

which is rapidly dominated by its largest diagonal element(s). If all the other diagonal elements were actually zero, then, in terms of the original basis, the resulting matrix would have rows (and columns) which are linear combinations of the eigenvectors corresponding to the largest eigenvalue.

Thus A^{2N} approximates such a matrix. Convergence goes as $(\lambda_1/\lambda_0)^{2N}$ where λ_0 is the largest eigenvalue and λ_1 is the next smaller one. Note that any scaling we do while taking powers to keep elements in bounds does not disturb the result, since we are looking at ratios of elements' magnitudes, not their absolute size.

We have made strong use of the symmetry of the matrix in the above discussion. The method is valid for a larger range of matrices, in particular for those in which there is a single eigenvector for a unique eigenvalue of largest magnitude essentially the same analysis applies. For an eigenvalue of multiplicity greater than one, there are problems in non-symmetric matrices in deciding whether the process has converged. However, the powers of the matrix will approach a sequence of matrices in which the columns are linear combinations of the eigenvectors of the eigenvalues of largest magnitude. One can see this by using a similar approach in choosing a basis from the eigenvectors (and bases of the eigenspaces where necessary) to obtain a slightly modified Jordan normal form, in which the diagonal elements are the eigenvalues and the off-diagonal elements are not necessarily one. The blocks without off-diagonal terms will behave as above, while those with off-diagonal terms will be dominated by them, leaving fewer independent vectors in the final matrix.

Similar arguments, of course, apply to simply taking successive powers, but taking squares produces more rapid convergence, and in eigenvalue problems where negative eigenvalues arise (unlike best-fit planes) taking a square prevents oscillation of sign. If instead of taking powers of the entire matrix, one followed just a single vector with those powers applied, and that vector had no component in the direction of the eigenvector of the largest eigenvalue, it would lead to the eigenvector of a smaller eigenvalue rather than the desired result.

Relationship to best-fit plane

As has been noted by others (Schomaker *et al.*, 1959), now consider a collection of points x_i of 'mass' m_i. The plane that best approximates these points may be taken as the one whose normal is in the direction providing maximal moment of inertia about the center of mass (or minimal r.m.s. deviation of mass from the plane). The 'mass' might be taken as true mass, or unit mass, or as an uncertainty measurement (Hamilton, 1961). In any case we need only compute an inertia tensor and find the eigenvector for its largest eigenvalue. Similarly, for the best line, the smallest eigenvalue is needed, which may be found by finding the largest eigenvalue of the inverse of the inertia tensor.

Specific details of the power method

Let m_i be the masses of points (x_i, y_i, z_i). Then the inertia tensor is

$$T = \begin{pmatrix} \sum m_i (y_i^2 + z_i^2) & -\sum m_i x_i y_i & -\sum m_i x_i z_i \\ -\sum m_i x_i y_i & \sum m_i (x_i^2 + z_i^2) & -\sum m_i y_i z_i \\ -\sum m_i x_i z_i & -\sum m_i y_i z_i & \sum m_i (x_i^2 + y_i^2) \end{pmatrix}.$$

Note that the matrix is symmetric.

Then we iterate on the following: (1) Square the matrix. (2) Multiply or divide by a suitable value, so that the elements stay within a reasonable range. (3) Stop when two successive iterations have column vectors which have not changed in direction by more than the desired error. Steps 2 and 3 fit together best if we normalize by a quantity explicitly computed from the elements of the matrix, say the trace of the matrix. After one squaring, the trace can be zero only if the eigenvalues of the square matrix are all zero. This involves fewer computations than use of the largest element.

Take one of the non-zero column vectors as an eigenvector of the largest eigenvalue. The eigenvalue itself may be found by applying the original matrix to such a vector, and computing the ratio of the lengths. It should be noted that the multiplication by the matrix corresponds precisely to a shift generated by taking the derivative for least-squares refinement of unit vectors to the desired plane. One may test for uniqueness of the eigenvector by finding the components of the remaining non-zero column vectors of the matrix perpendicular to the one chosen.

References

HAMILTON, W. C. (1961). Acta Cryst. **14**, 185–189.
NATIONAL PHYSICAL LABORATORY (1957). Modern Computing Methods, Notes on Applied Science, No. 16, p. 30. London: Her Majesty's Stationery Office.
SCHERINGER, C. (1971). Acta Cryst. B**27**, 1470–1472.
SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). Acta Cryst. **12**, 600–604.

The Debye–Waller Factor of Lead from 296 to 550 K

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The Debye–Waller factor of lead has been measured by neutron diffractometry at five temperatures in the range 296–550 K. The results are analysed in terms of a central-force pair-interaction model, and the anharmonic pair potential obtained is significantly different from that derived from previous X-ray measurements. Several methods of calculating TDS contributions to powder diffraction peaks are examined, and their results are compared.

1. Introduction

In a recent study of the X-ray Debye temperatures $\Theta_D(T)$ of cubic materials, Killean (1974) has shown that the variation of the Debye–Waller factor, $B(T)$, of aluminum with temperature T can be adequately described by nearest-neighbour central-force (NNCF) pair interactions. This work has been extended to other f.c.c. metals (Killean & Lisher, 1975a), and to elastic-constant Debye temperatures of f.c.c. and b.c.c. elements (Killean & Lisher, 1975b). In all cases good agreement was found between theoretical predictions and the experimental data. A new criterion for melting was proposed (Killean & Lisher, 1975b) and this criterion, when applied to the elastic-constant data, yielded excellent agreement with the observed melting temperatures for the majority of materials studied. This melting criterion, however, was less successful when used with the X-ray data and it was not clear whether this was due to errors inherent in the X-ray measurements, or to shortcomings in the proposed theory. To resolve this point, a series of neutron diffraction studies of f.c.c. heavy metals is being undertaken, and the first of these experiments is reported in the present paper.

The neutron diffraction technique has several advantages over the X-ray method as a means of measuring absolute Debye–Waller factors. In the X-ray case there are problems such as uncertainties in the atomic scattering factors, extinction and specimen misalignment which prevent an accurate determination of $B(T)$ directly from the slope of a 'Wilson plot' of ln I against $\sin^2 \theta/\lambda^2$. Several methods of minimizing the errors in the X-ray technique have been proposed, but these generally presuppose the knowledge of a relation between $\Theta_D(T)$ and T and are thus unsatisfactory as a means of determining absolute Debye temperatures.

A Wilson plot may be used in the analysis of neutron diffraction data from powder samples, since the constancy of nuclear scattering lengths and the elimination of significant extinction in the specimen remove two principal sources of error which are θ-dependent. A major drawback of the powder technique is the possibility of preferred orientation, and subsequent large changes in the orientation of the grains due to sintering at high temperatures. This effect may be reduced by annealing the powder before performing the diffraction measurements with the sample rotating or oscillating.

2. Experimental

The sample used in the present study was lead powder, of maximum particle size 150 μm and purity 99·999%, which was obtained commercially from Goodfellow Metals Ltd. During the diffraction measurements this powder was contained in an aluminum can of diameter 16 mm and wall thickness 0·25 mm.