Acta Cryst. (1985). **A41**, 274–278

Solving Crystal Structures Using Several Wavelengths from Conventional Sources. Anomalous Scattering by Holmium

By Gervais Chapuis

Institut de Cristallographie, Université de Lausanne, BSP, 1015 *Lausanne, Switzerland*

and David H. Templeton and Lieselotte K. Templeton

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720, *USA*

(*Received* 2 *August* 1984; *accepted* 28 *November* 1984)

Abstract

The anomalous scattering terms for trivalent holmium are measured for Cu $K\alpha_1$, $K\alpha_2$ and $K\beta$ radiation in diffraction experiments with a crystal of HoNa(edta).8H_2O. Intensities at these wavelengths and at Mo $K\alpha$ are used to calculate amplitudes and the phase difference for the waves scattered by holmium and by the rest of the structure to test the multiple-wavelength method of diffraction phase determination. Relative phases are determined with a mean accuracy of 44° for 759 high-angle reflections. A similar calculation for the analogous Sm crystal using synchrotron-radiation data gives the phase difference with an average error of 5°.

Introduction

Anomalous scattering has long been recognized as a source of helpful information for solving crystal structures by diffraction methods. For most substances at most X-ray wavelengths the effects are rather small, yet they are useful and are widely used in an accessory manner in one-wavelength studies, and of course to establish absolute configuration. More information can be obtained by using more than one wavelength. Near an absorption edge the complex scattering factor changes with wavelength. These changes may be quite large, for example as much as 30 electrons atom^{-1} near some L_3 edges (Templeton, Templeton, Phizackerley & Hodgson, 1982). They may induce substantial variation of the diffracted intensities depending on the wavelength of the incident beam. Various authors (*e.g.* Herzenberg & Lau, 1967, and references cited therein; Karle, 1980) have described the basic principles for obtaining information on diffraction phases from Friedel pairs of measurements at different frequencies. Hoppe & Jakubowski (1975) demonstrated the method with erythrocruorin using two wavelengths. These effects can be very large in neutron diffraction in special cases. Their usefulness with a single wavelength of neutrons was demonstrated by Macdonald & Sikka (1969) and Sikka & Rajagopal (1975). They were applied to the solution of the structure of NaSm(edta).8H_2O with measurements at three neutron wavelengths by Koetzle & Hamilton (1975). Most of the recent work on the multiple-wavelength method has been in the context of synchrotron radiation, because it permits access to the largest effects for X-rays. The method has not yet been very widely exploited, however, in part because access to synchrotron radiation is still limited, and perhaps in part for lack of recognition of how much can be done with ordinary laboratory sources.

Holmium is a special case because its L_3 absorption edge (1·5368 Å) is very close to Cu $K\alpha$ radiation, so close that the holmium scattering factor is not the same for $K\alpha_1$ (1·5406 Å) and $K\alpha_2$ (1·5444 Å). Furthermore, its L_2 edge (1·3905 Å) is only 0·0017 Å below the wavelength of Cu $K\beta_{1,3}$ (wavelengths from Bearden, 1967). Thus three effectively different wavelengths are available from a single anode. The purposes of the present work were to measure the scattering factor of holmium at these wavelengths using an ordinary X-ray source, to test its application in the multiple-wavelength method of phase determination, and to explore some alternative procedures for this method.

Algebraic theory

For simplicity of notation we consider a structure in which the scattering factor of only one kind of atom changes with wavelength, and assume that f'' is negligible for other atoms. This treatment is adequate for the present work. More complicated cases need more algebra and sometimes more wavelengths for effective solution, but do not require any fundamental change of the theory. We write the structure factor as the sum of an anomalous (A) part and a normal (N) part:

$$\begin{aligned}F(\mathbf{h}) &= F_A+F_N\\ &=\sum_{j=1}^{m}(f_j^0+f_j'+if_j'')\exp(2\pi i\mathbf{h}\mathbf{x}_j)\\ &\quad+\sum_{j=m+1}^{M}f_j^0\exp(2\pi i\mathbf{h}\mathbf{x}_j).\end{aligned}\qquad(1)$$

0108-7673/85/030274-05$01.50

With only one kind of anomalous atom we can drop the subscripts on f' and f'', which are the only quantities in this expression that depend on wavelength. By definition:

$$f = f^0 + f' + if'' = f^0 g \exp(i\delta), \tag{2}$$

where

$$g \cos \delta = (f^0 + f')/f^0 \tag{2a}$$

and

$$g \sin \delta = f''/f^0. \tag{2b}$$

We define further:

$$F_A^0 = \sum_{j=1}^{m} f^0 \exp(2\pi i \mathbf{h}\mathbf{x}_j) = |F_A^0| \exp(i\varphi_A^0). \tag{3}$$

Then,

$$F = |F_A^0| g \exp[i(\delta + \varphi_A^0)] + |F_N| \exp(i\varphi_N), \tag{4}$$

where φ_N is the phase of F_N. We introduce the new variable

$$\Delta = \varphi_A^0 - \varphi_N \tag{5}$$

and multiply (4) by its complex conjugate to obtain

$$|F|^2 = |F_N|^2 + g^2|F_A^0|^2 + 2g \cos \delta |F_A^0|\,|F_N| \cos \Delta$$
$$- 2g \sin \delta |F_A^0|\,|F_N| \sin \Delta. \tag{6}$$

This expression is linear in the four terms

$$x_1 = |F_N|^2,$$
$$x_2 = |F_A^0|^2,$$
$$x_3 = |F_A^0|\,|F_N| \cos \Delta$$

and

$$x_4 = |F_A^0|\,|F_N| \sin \Delta, \tag{7}$$

but subject to the additional condition

$$x_1 x_2 = x_3^2 + x_4^2. \tag{8}$$

An expression similar to (6) has been derived by Karle (1980). It is easy to show that the expression corresponding to (6) for $F(-\mathbf{h})$ differs only by the sign of the coefficient of x_4. Denoting by $|F_+|$ and $|F_-|$ the magnitudes of a Friedel pair $F(\mathbf{h})$ and $F(-\mathbf{h})$, one can derive

$$|F_+|^2 - |F_-|^2 = -4gx_4 \sin \delta, \tag{9a}$$

$$|F_+|^2 + |F_-|^2 = 2(x_1 + g^2 x_2 + 2gx_3 \cos \delta). \tag{9b}$$

One sees that x_4 is directly proportional to the Friedel (or Bijvoet) intensity difference and with a known proportionality factor. The other variables depend linearly on the sum of the Friedel intensities, but subject to condition (8).

In principle it is possible to determine uniquely the three variables of interest, namely $|F_N|$, $|F_A^0|$ and the angle Δ with three observations at various wavelengths or two observations at different wavelengths and one Friedel pair. Unfortunately, the experimental observations are subject to errors, and the problem is best solved by optimization with redundant data. It is important to realize that the method gives only a phase difference Δ, defined by (5), rather than a phase relative to a chosen origin. If the heavy (anomalous) atom positions are known, φ_A^0 can be calculated. If they are not known, they can be found with a Patterson map or direct methods using the set of $|F_A^0|$, if it is accurate enough and complete enough.

The solution of a set of equations (6) requires that the observed structure amplitudes are on a consistent scale. Scale factors can be obtained from Wilson statistics, aided by the fact that temperature factors are the same for all wavelengths if the temperature is constant. One must remember, however, that

$$\langle |F|^2 \rangle = \sum f^2 = \sum g^2 (f^0)^2 \tag{10}$$

is not the same at all wavelengths because of the factors g. This matter has also been discussed by Karle (1984).

Experimental

The structure of NaHo(edta).8H$_2$O, edta = ethylenediaminetetraacetate, has been determined by Templeton, Templeton & Zalkin (1985) using Mo $K\alpha$ radiation. Crystal data: Na[Ho(C$_{10}$H$_{12}$N$_2$O$_8$)].8H$_2$O, monoclinic, $Fd11$, $a = 19{\cdot}333\,(3)$, $b = 35{\cdot}366\,(6)$, $c = 12{\cdot}106\,(2)$ Å, $\alpha = 90{\cdot}40\,(10)$°, $Z = 16$. The unit cell and space-group symbol are chosen for an unconventional setting of space group Cc to preserve the close similarity of cell dimensions and atomic coordinates with respect to the orthorhombic $Fdd2$ structure of a series of analogous rare-earth salts (Templeton, Templeton, Zalkin & Ruben, 1982, and references therein).

Diffraction intensities were measured with Cu $K\alpha$ and $K\beta$ radiation for a crystal with 8 faces, 0·41 × 0·45 × 0·53 mm, Enraf–Nonius CAD-4 diffractometer with graphite monochromator, θ–2θ scan technique. Correction factors for absorption by the analytical method (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973) ranged from 3·4 to 7·6 for $K\alpha$ and 6·5 to 33 for $K\beta$. Measurements included both members of each Bijvoet pair in the angular ranges indicated in Table 1.

Damage induced by radiation in crystals of this holmium compound is indicated by changes in the α angle (Templeton, Templeton & Zalkin, 1985). This angle was 90·40 (1)° at the start of the Cu $K\alpha$ experiment and 90·28 (1)° after the end, in close correspondence with the change observed in the collection of Mo $K\alpha$ data. By the end of the Cu $K\beta$ experiment, α had changed to 90·11 (1)°. Thus the various measurements refer to slightly different structures, introducing small errors of unknown magnitude.

Table 1. *Data for* NaHo(*edta*).8H_2O

	Mo $K\alpha$	Cu $K\beta$	Cu $K\alpha_1$	Cu $K\alpha_2$
λ (Å)	0·7107	1·3922	1·54056	1·54439
μ (cm^{-1})	39·7	154	81·5	81·5
$[(\sin\theta)/\lambda]_{\min}$	0·11	0·04	0·50	0·50
$[(\sin\theta)/\lambda]_{\max}$	0·60	0·60	0·59	0·59
Number of reflections $[I > \sigma(I)]$	4843*	6285	1940	1940
R	0·026	0·050	0·098	0·117
f' (expt)	—	−12·9 (1)	−16.0 (2)	−13·9 (3)
f' (theor)†	−0·71 −0·67‡	−11·88	−15·41	−14·09
f'' (expt)	4·9 (1)	9·3 (1)	3·9 (2)	3·6 (3)
f'' (theor)†	4·67 4·68‡	8·75	3·70	3·72

* Range of h limited to 0-12.
† Calculated by program of Cromer (1983).
‡ Cromer & Liberman (1970) for Mo $K\alpha_1$.

For the separation of the intensity into the $K\alpha_1$ and $K\alpha_2$ components, the 96 values of each scan measurement were fitted to a sum of two Gaussian curves and a constant term:

$$I(t) = c_1 + c_2 \exp[-a_1(t-a_2)^2] + c_3 \exp[-a_3(t-a_4)^2]. \quad (11)$$

The linear (c_i) and non-linear (a_i) constants were obtained by multiple non-linear regression (*VARPRO*, 1979). The components were calculated from the expressions

$$I(K\alpha_1) = c_2(\pi/a_1)^{1/2}, \quad I(K\alpha_2) = c_3(\pi/a_3)^{1/2}, \quad (12)$$

which represent the areas delimited by the background line and the Gaussian curves. It is interesting to note that the ratio $I(K\alpha_1)/I(K\alpha_2)$ for some reflections differs significantly from the usual value of 2; a few are smaller than 0·5 or larger than 6!

The solution of a set of equations (6) also requires knowledge of the anomalous scattering factors for the Ho atom. They were determined by least-squares refinement of each data set and are listed in Table 1. For the two Cu $K\alpha$ sets only the scale and anomalous parameters were refined with other parameters fixed at the values found with the Mo $K\alpha$ data. For the Cu $K\beta$ set the anomalous parameters were refined along with the coordinates and anisotropic thermal parameters of the Ho atoms. For Mo $K\alpha$ we used values from Cromer & Liberman (1970).

The three copper data sets and the molybdenum data (Templeton, Templeton & Zalkin, 1985) were used to test the multiple-wavelength method. Multiple linear regression was used to find estimates of x_1, x_2, x_3 and x_4, subject to constraint (8). Initial values were all taken as zero after tests showed that more elaborate techniques did not improve convergence. The structure amplitudes $|F_N|$ and $F_A^0|$ and the relative phase Δ were then derived from (7). This was done for each reflection for which a Bijvoet pair was included in at least three of the data sets. Among the 763 groups satisfying this condition, the relative phases and amplitudes for only four reflections could not be determined because solutions of the regression were physically unrealistic. The most frequent number of iterations necessary to attain convergence was 6; 80% of the refinements converged with less than 16 iterations. A damping factor of 0·5 was introduced beyond 30 iterations to accelerate convergence.

Analysis of the results

The large number of least-squares cycles needed to obtain convergence is due to the high correlation between the two variables x_2 and x_3. The correlation coefficients derived from the covariance matrix lie between −0.97 and −0.98. The correlation coefficients for x_2, x_4 and x_3, x_4 are practically zero. This characteristic shows that in essence our problem has two independent variables, namely $f(x_2, x_3)$ and $f(x_4)$. Geometrically, the refinement amounts to finding the two sides of a right triangle knowing the hypotenuse. One side is determined by the sum, the other by the difference, of a Bijvoet pair as given by (9). The additional step of separating $f(x_2, x_3)$ into $f(x_2)$ and $f(x_3)$ is more difficult; one is looking for a point on the side which is not well defined.

The ratio $R = \sum[|F_A^0|_c - |F_A^0|_t]/\sum|F_A^0|_c = 0{\cdot}18$ shows a fair agreement between the values obtained from this refinement (c) and those calculated from the known structure (t). The corresponding ratio for F_N is 0·48. This higher value is associated with the large number of small amplitudes. The error in the determination of Δ is directly linked to the magntiudes of F_N. The standard deviation calculated from the least-squares refinement lies typically in the range between 20 and 30°. The average values of $\varepsilon = |\Delta_c - \Delta_t|$ is 44°. The percentage cumulative distribution of the reflections *vs* ε is plotted in Fig. 1. For 60% of the 759 reflections, ε is less than 40°. For comparison, we have done a similar calculation for the nearly isomorphous Sm derivative using data measured at four wavelengths with synchrotron radiation by Templeton, Templeton, Phizackerley & Hodgson (1982). This time the mean difference $\langle\varepsilon\rangle$ is 5° for 311 reflections. The results are also plotted in Fig. 1. The dramatic improvement in this case is due both to the much larger range of f' and f'' values (which range from −8·9 to −31·5 and 4·4 to 28·9) and to the greater accuracy of the intensity measurements. The accuracy of the holmium data was degraded both by the difficulty of resolving the $K\alpha_1$ and $K\alpha_2$ contributions and by the progressive radiation damage.

These high-angle data for the Ho compound have been used to calculate a Fourier map with $[|F_N| \exp(i\varphi_N)]$ as coefficients. The phase φ_N was obtained from (5) with φ_A^0 replaced by the value calculated from the known positions of the Ho atoms. In this map nine of the first ten peaks, and three more of the next ten, are at correct light-atom positions. Four of the other eight are near holmium positions, indicating imperfect subtraction of the heavy-atom contribution. The remaining four peaks, and the majority of smaller ones, do not correspond to atomic positions. For comparison, a theoretical Fourier map with the same terms but with coefficients calculated from the light atoms of the known structure indicates that the 40 largest peaks correspond to atoms.

Concluding remarks

The differences between experimental and theoretical values of f' and f'', Table 1, are explained by several factors. For wavelengths this close to an absorption edge the scattering factor depends on the chemical state of the atom, here the +3 oxidation state. The value of f' is sensitive to the precise wavelength of the absorption edge, which is likely to change with oxidation state and may not be the same as the value used in the theory. It is also sensitive to the resonance structure of the absorption edge, which in this case includes a very strong white line and which is disregarded in the theoretical model, as is the finite level width of the edge. These experimental values are relevant to finite scattering angles and therefore may differ by a few percent from the zero-angle values calculated by theory. While the wavelengths of the characteristic X-ray lines are stated with great precision, the natural widths of these lines are appreciable. The experimental scattering factors actually correspond to some kind of average over each line profile. The effect on the values may not be negligible so close to an absorption edge. Finally, it is difficult to judge the accuracy of the theoretical model.

We find the results of the phase-determination tests to be very encouraging. The samarium experiment is an example of overkill because the anomalous scattering tends to dominate the intensity data. The phase accuracy of *ca* 45° in the holmium experiment is sufficient to lead to a correct solution of a structure even with inaccurate initial values of $|F_N|$. There are several ways in which the experiment can be improved. Obviously it would better without the radiation damage; however, this damage may add realism to this experiment as a stand-in for a protein. We operated the diffractometer in a routine manner, and the α_1 and α_2 intensities are not very accurate. More elaborate monochromator techniques could achieve a better separation of these two components, even for the low-angle reflections that are relevant to serious phasing problems. A simpler way to phase low-angle reflections is to use a weighted-average scattering factor with an unresolved $K\alpha$ doublet and be content with only three wavelengths. It seems likely that this method would be successful, but it remains to be tested. The important things for phasing (besides accurate intensities) are at least one large value of f'' (given here by Cu $K\beta$) and a large range of values of f' (given here by Mo $K\alpha$ and Cu $K\alpha$). Attempts to determine phases with only the three copper wavelengths were not very successful because the range of f' was not large enough.

Improved estimates of Δ can probably be obtained with a recycling procedure. Once the partial structure of the anomalous atoms is determined, calculated values of x_2 can be used. There are then only two independent unknowns, and the problem of large correlations disappears.

While holmium is a special case, it is not unique. Lanthanum has a similar relationship to Cr $K\alpha$ and $K\beta$, while its f' is close to zero for Cu $K\alpha$ or Mo $K\alpha$. Europium used with $K\alpha$ radiation of cobalt, copper and molybdenum may be an even better combination. Still other combinations exist that may be useful.

We believe that conventional sources merit more attention than they have received for multiple-wavelength phase determination. However, it is obvious that synchrotron radiation has a strong advantage if convenient access to it can be achieved.

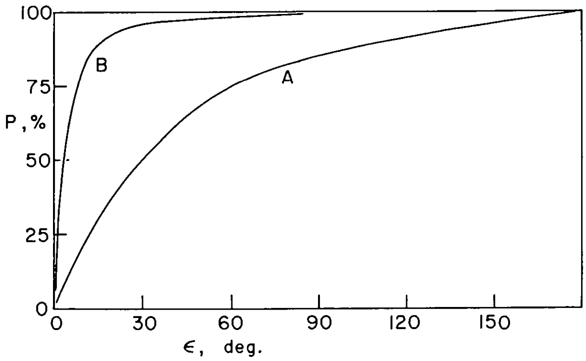

Fig. 1. Cumulative percentage distribution of the reflections as a function of $\varepsilon = |\Delta_c - \Delta_t|$, the error in relative phase: *A* Ho salt with conventional X-rays; *B* synchrotron data (Templeton, Templeton, Phizackerley & Hodgson, 1982) for Sm salt.

We thank Dr Allan Zalkin and Dr Frederick J. Hollander for helpful assistance. This work was supported by the Fondation Herbette, Université de Lausanne, by the National Science Foundation under grant No. CHE-8217443 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract No. DE-AC03-76SF00098. Facilities of the UC Berkeley X-ray Crystallographic Facility (CHEXRAY) were used.

References

BEARDEN, J. A. (1967). *Rev. Mod. Phys.* **39**, 78–124.

CROMER, D. T. (1983). *J. Appl. Cryst.* **16**, 437.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

HERZENBERG, A. & LAU, H. S. M. (1967). *Acta Cryst.* **22**, 24-28.
HOPPE, W. & JAKUBOWSKI, U. (1975). *Anomalous Scattering*, edited by S. RAMASESHAN & S. C. ABRAHAMS, pp. 437-461. Copenhagen: Munksgaard.
KARLE, J. (1980). *Int. J. Quantum Chem. Symp.* **7**, 357-367.
KARLE, J. (1984). *Acta Cryst.* **A40**, 1-4.
KOETZLE, T. F. & HAMILTON, W. C. (1975). *Anomalous Scattering*, edited by S. RAMASESHAN & S. C. ABRAHAMS, pp. 489-502. Copenhagen: Munksgaard.
MACDONALD, A. C. & SIKKA, S. K. (1969). *Acta Cryst.* **B25**, 1804-1811.
MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014-1018.
SIKKA, S. K. & RAJAGOPAL, H. (1975). *Anomalous Scattering*, edited by S. RAMASESHAN & S. C. ABRAHAMS, pp. 503-514. Copenhagen: Munksgaard.
TEMPLETON, L. K. & TEMPLETON, D. H. (1973). Proc. Am. Crystallogr. Assoc. Meet., Storrs, CT, Abstr., p. 143.
TEMPLETON, L. K., TEMPLETON, D. H., PHIZACKERLEY, R. P. & HODGSON, K. O. (1982). *Acta Cryst.* **A38**, 74-78.
TEMPLETON, L. K., TEMPLETON, D. H. & ZALKIN, A. (1985). *Acta Cryst.* **C41**, 355-358.
TEMPLETON, L. K., TEMPLETON, D. H., ZALKIN, A. & RUBEN, H. W. (1982). *Acta Cryst* **B38**, 2155-2159.
VARPRO (1979). *Multiple Nonlinear Regression Program.* Computer Center, Lawrence Berkeley Laboratory, Berkeley.

Acta Cryst. (1985). **A41**, 278-280

Nomenclature for Crystal Families, Bravais-Lattice Types and Arithmetic Classes

Report of the International Union of Crystallography *Ad-Hoc* Committee on the Nomenclature of Symmetry*

BY P. M. DE WOLFF (Chairman), *Department of Applied Physics, Delft University of Technology, Lorentzweg* 1, 2628 *CJ Delft, The Netherlands*, N. V. BELOV,† *Institute of Crystallography, Academy of Sciences of the USSR, Leninsky pr.* 59, *Moscow* 117333, *USSR*, E. F. BERTAUT, *Laboratoire de Cristallographie, CNRS Grenoble*, 25 *Avenue des Martyrs, BP* 166*X Centre de Tri*, 38042 *Grenoble CEDEX, France*, M. J. BUERGER, *PO Box* 361, *Lincoln Center, MA* 01773, *USA*, J. D. H. DONNAY, *Department of Geological Sciences, McGill University*, 3450 *University Street, Montreal, Canada H*3*A* 2*A*7, W. FISCHER, *Institut für Mineralogie, Petrologie und Kristallographie der Philipps-Universität, Lahnberge, D*-3350 *Marburg* (*Lahn*), *Federal Republic of Germany*, TH. HAHN, *Institut für Kristallographie, RWTH, Templergraben* 55, *D*-5100 *Aachen, Federal Republic of Germany*, V. A. KOPTSIK, *Moscow State University, Department of Physics, Leninskiye Gory, Moscow* 117234, *USSR*, A. L. MACKAY, *Department of Crystallography, Birkbeck College, London W*1*E* 7*HX, England*, H. WONDRATSCHEK, *Institut für Kristallographie, Universität, Kaiserstrasse* 12, *D*-7500 *Karlsruhe, Federal Republic of Germany*, A. J. C. WILSON (*ex officio*, IUCr Commission on *International Tables*), *Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB*2 1*EW, England* and S. C. ABRAHAMS (*ex officio*, IUCr Commission on Crystallographic Nomenclature), *AT&T Bell Laboratories, Murray Hill, NJ* 07974, *USA*

(*Received* 13 *August* 1984; *accepted* 13 *November* 1984)

Abstract

Standard symbols representing crystal families, two- and three-dimensional Bravais-lattice types and arithmetic classes are recommended for use by the IUCr. The six crystal families are designated by lower-case letters. The family letter in the symbol of each of the 14 lattice types is followed by an upper-case letter to distinguish different lattice types within the family. Arithmetic classes are indicated by modified symbols of the corresponding symmorphic space groups.

Crystal families

Six lower-case letters, which originate from words denoting the shape of commonly used unit cells, are recommended as the standard designation of *crystal families* (Table 1). A 'crystal family' is a well defined and unambiguous concept in crystallography [*International Tables for Crystallography* (1983), sections 2.1 and 8.2.6]. Comparing the classification into crystal families with existing classifications into 'crystal systems', it is noted that they coincide except for the hexagonal family in three dimensions, which contains all 'hexagonal', 'trigonal' and 'rhombohedral' space groups. Although this set is often regarded as a single 'crystal system' in the American and Russian literature, other widespread usage divides it into two different systems. Therefore, association of the lower-

---

* Appointed 18 March 1980 under ground rules outlined in *Acta Cryst.* (1979), **A35**, 1072. Final Report accepted 17 August 1984 by the IUCr Commission on Crystallographic Nomenclature and 13 November 1984 by the Executive Committee.

† Deceased 6 March 1982.

0108-7673/85/030278-03$01.50