INTERNATIONAL UNION OF CRYSTALLOGRAPHY

INTER CONGRESS CONFERENCE

ON

ANOMALOUS SCATTERING

PROGRAMME & ABSTRACTS

22 - 26 APRIL 1974

MADRID, SPAIN

EDICIONES DE LA UNIVERSIDAD DE BARCELONA

BARCELONA (SPAIN)

The Executive Committee of the International Union of Crystallography has agreed to sponsor publication of the Proceedings of the Conference in book form. The book will be printer in Parma, Italy with the page format used by Crystal Structure comunications.

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MADRID, SPAIN

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Monday - April 22, 1974:

INAUGURATION

9.00- 9.05 S.C. Abrahams

9.05- 9.10 M. Font Altaba

9.10- 9.25 E. Gutierrez-Rios

9.25- 9.30 S. Ramaseshan

Chairman: S. Garcia-Blanco

9.30-10.20 1 Opening lecture: Use of anomalous scattering in structure analysis
A.F. Peerdeman, Laboratorium Voor Kristal Chemie, Catharjnesingel, Utrecht, The Netherlands.

10.20-10.50 Coffee break

DISPERSION CORRECTIONS-THEORETICAL COMPUTATIONS

10.50-11.15 2 Theoretical computations of X-ray dispersion corrections
H. Wagenfeld, Fritz-Haber-Institut der Max Planck Gesselschaft, Berlin, Dahlem, W.Germany.

11.15-11.40 3 The sign of $\Delta f''$ according to classical, semiclassical and quantum field calculations
M.P. Groenewege, Algemene Chemie, Transitorium III, Utrecht, The Netherlands.

11.40-12.05 4 The dependence of dispersion corrections on the angle of scattering
A.C. Hazell, University of Aarhus, Denmark.

12.05-12.30

12.30-14.00 Lunch break

DISPERSION CORRECTIONS-EXPERIMENTAL DETERMINATIONS

Chairman: S.C. Abrahams

14.00-14.50 5 Determination of dispersion corrections by X-ray interferometry
M. Hart, H.H. Wills Physics Laboratory, University of Bristol, England.

14.50-15.15 6 The determination of Hönl's corrections for copper using a perfect crystal and continuous X-rays
A. Freund, Institut Max von Laue-Paul Langevin, Grenoble Cedex, France.

15.15-15.45 Coffee break

15.45-16.35 7 Experimental determination of dispersion corrections
B. Post, Polytechnic Institute of New York, New York, U.S.A.

16.35-17.00 8 The determination of $\Delta f''$ for heavy atoms
D.W. Engel* and M. Sturm**
*University of the O.F.S., Bloemfontein, South Africa,
**Max-Planck Institute fur Eiweiss-und Leder forschung, München, Germany (BRD).

17.00-17.25

Tuesday - April 23, 1974:

ANOMALOUS SCATTERING-NOVEL APPLICATIONS

Chairman: R.L. Mössbauer

9.00- 9.50 9 Implications of non-kinematic and inelastic scattering of electrons for structure analysis
J.M. Cowley, Arizona State University, Tempe, Arizona, U.S.A.

9.50-10.15 10 Anomalous dispersion effects in large crystals
C.A. Wallace, Marconi-Elliott Avionic Systems, Borehamwood, U.K.

10.15-10.45 Coffee break

10.45-11.35 11 A unified approach to anomalous scattering and some novel applications of the multiple wavelength method
S. Ramaseshan, National Aeronautical Laboratory, Bangalore, India.

11.35-12.00 12 Identification of atomic environments by anomalous X-ray scattering and other perturbation diffraction methods
J.F. Duncan, A.G. Freeman and J.H. Johnston, Victoria University of Wellington, New Zealand.

12.00-12.25 13 Contributions to X-ray diffuse scattering measurements from an inelastic scattering associated with anomalous dispersion
C.J. Sparks Jr., Oakridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

12.30-14.00 Lunch break

ABSOLUTE CONFIGURATION AND TENSORIAL PROPERTIES

Chairman: S. Hosoya

14.00-14.50 14 Absolute sign determination of tensor properties in relation to structure
S.C. Abrahams, Bell Laboratories, New Jersey, U.S.A.

14.50-15.15 15 "Ferroelectric X-ray anomalous scattering effect" applied to probing tridimensional domains in ferroelectrics
F.C. Lissalde* and J.C. Peuzin**
*C.N.R.S., Laboratoire des Rayons, Grenoble Cedex, France.
**C.E.A.-C.E.N.-G, LETI/CRM, Grenoble Cedex, France.

15.15-15.45 Coffee break

15.45-16.35 16 Application of anomalous scattering to chirality (induced noncentrosymmetry)
D. Rogers, Imperial College of Science and Technology, London, England.

16.35-17.00 17 Anomalous dispersion and diffraction symmetry
H. Iwasaki, The Institute of Physical and Chemical Research, Saitama, Japan.

17.00-17.25 18 The anomalous dispersion effect in $LiGaO_2$ at two wavelengths
M. Marezio, D. Tranqui and J.J. Capponi
Laboratoire des Rayons X- C.N.R.S - Grenoble Cedex, France.

Wednesday - April 24, 1974:

Excursion to Toledo

Thursday - April 25, 1974:

ANOMALOUS SCATTERING-INTENSITY MEASUREMENTS

Chairman: W. Hoppe

9.00- 9.50 19 Anomalous scattering measurements and amplitude and phase determination with continuous X-ray radiation
S. Hosoya, Institute for Solid State Physics, Tokyo, Japan.

9.50-10.15 20 Accurate intensity measurement of X-ray intensities and Bijvoet differences from an extended crystal face
Z. Barnea, University of Melbourne, Parkville, Australia.

10.15-10.45 Coffee break

10.45-11.35 21 Intensity measurements
H. Hope, University of California, Davis, U.S.A.

11.35-12.25 22 Anomalous scattering and accuracy of intensities
A. Vos, Laboratorium voor Structur chemie, The Netherlands.

12.30-14.00 Lunch break

16.35-17.00 17 Anomalous dispersion and diffraction symmetry
H. Iwasaki, The Institute of Physical and Chemical Research, Saitama, Japan.

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A. Vos, Laboratorium voor Structur chemie, The Netherlands.

12.30-14.00 Lunch break

REFINEMENT PROCEDURES AND ERRORS IN ATOMIC PARAMETERS

Chairman: G. Kartha

14.00-14.25 23 Neglect of dispersion and apparent atomic parameters
A.J.C. Wilson, University of Birmingham, Birmingham, U.K.

14.25-14.50 24 Anomalous dispersion effects on ΔF synthesis and least-squares refinement of centrosymmetric structures
G.Gilli* and A.Del Pra**
*Istituto Chimica, Universita di Ferrara, Italia,
**Istituto di Chimica Organica, Universita di Padova, Italia.

14.50-15.15 25 Errors in various parameters caused by neglect of anomalous dispersion effect
A.K. Singh, Institute of Geophysics and Planetary Physics, University of California, Los Angeles, U.S.A.

15.15-15.45 Coffee break

15.45-16.35 26 The effect of anomalous scattering on atomic parameters
R.Srinivasan, Centre of Advanced Study in Physics, Madras, India.

16.35-17.00 27 Use of dispersion effects in structure solution
P.J. Black, University of Birmingham, Birmingham, England.

17.00-17.25 28 Accurate intensity measurements including anomalous scattering
B.W. Batterman, Cornell University, Ithaca, New York, U.S.A.

Conference Banquet

Friday, April 26, 1974:

ANOMALOUS SCATTERING AND THE STRUCTURE ANALYSIS OF MACROMOLECULES

Chairman: A.J.C. Wilson

9.00- 9.50	29	The application of anomalous dispersion methods to the structure analysis of macromolecules R.L. Mössbauer, Institute Laue-Langevin, Grenoble, France.
9.50-10.15	30	The use and limitations of anomalous dispersion data from protein crystals E.J. Dodson, G.G. Dodson, P.R. Evans and S. French, Laboratory of Molecular Biophysics, Oxford, England.
10.15-10.45		Coffee break
10.45-11.35	31	The determination of phases of erythrocruorin using the two wavelength method with iron as anomalous scatterer W. Hoppe, Max-Planck-Institut fur Biochemie, München, W.Germany.
11.35-12.25	32	Use of anomalous scattering in protein structure analysis G. Kartha, Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, New York, U.S.A.
12.30-14.00		Lunch break

Chairman: A. Vos

14.00-14.25	33	Anomalous scattering in protein structure analysis K.D. Watenpaugh, L.C. Sieker and L.H.Jensen University of Washington, Seattle, Washington, U.S.A.
14.25-14.50	34	Anomalous scattering in protein structure analysis S. Parthasarathy, University of Madras, Madras, India.

14.50-15.15 35 Use of anomalous scattering in structure solution
M. Mammi, Istituto di Chimica Organica, Dell'Universita, Padova, Italy.

15.15-15.45 Coffee break

STRUCTURE DETERMINATION USING NEUTRON ANOMALOUS SCATTERING

15.45-16.35 36 Neutron Anomalous scattering to phase protein structures
B.P. Schoenborn, Brookhaven National Laboratory, Upton, New York, U.S.A.

16.35-17.00 37 Neutron diffraction study of NaSm EDTA. $8H_2O$: An evaluation of methods of phase determination based on three wavelength anomalous dispersion data
T.F. Koetzle* and W.C. Hamilton**
*Brookhaven, National Laboratory, Upton, Newyork, U.S.A.
**Deceased.

17.00-17.25 38 Application of neutron anomalous dispersion in the structure determination of cadmium tartrate monohydrate
S.K. Sikka and H. Rajagopal, Bhabha Atomic Research Centre, Bombay, India.

ABSTRACTS

USE OF ANOMALOUS SCATTERING IN STRUCTURE ANALYSIS

A F Peerdeman , Laboratorium Voor Kristal Chemie
Der Rijkuniversiteit, Catharijnesingel , 51/52 , Utrecht , The Netherlands.

(Abstract not yet received)

DISPERSION CORRECTIONS-THEORETICAL COMPUTATIONS

Chairman: S. GARCIA-BLANCO

Monday, 11h.15.

THEORETICAL CONPUTATIONS OF X-RAY DISPERSION CORRECTIONS

H. Wagenfeld, Fritz-Haber-Institut der Max-Planck-Gesellschaft
Berlin-Dahlem

Several papers have been published concerning calculations of dispersion corrections for X-ray atomic scattering factors. Each dispersion correction consists of a real part $\triangle f'$ and an imaginary part $\triangle f''$. These quantities are connected to one another for each atomic electron by a Kronig-Kramer dispersion relation. Computations of $\triangle f'$ and $\triangle f''$ presume for each atomic electron the knowledge of the oscillator density or the photoelectric absorption cross section. There have been mainly three different approaches for calculations of dispersion corrections:

1) Hönl (1933) calculated the matrix elements for the transition probabilities which are contained in the oscillator strengths and the photoelectric absorption cross sections by means of hydrogen-like eigenfunctions. He expanded these matrix elements into electromagnetic multipole transitions and so obtained the angular dependence of $\triangle f'$ and $\triangle f''$ as well. The initial calculations have been restricted to the two electrons of the K-shell only. An extention to other electron shells and numerical computations have been carried out by other authors.

2) Parratt and Hempstead (1954) assumed for the photoelectric absorption cross sections semiempirical expressions. If these expressions are known, then the computations of $\triangle f'$ and $\triangle f''$ are straightforward. Such computations including some improvements have been made by several authors.

3) Cromer and Liberman (1970) used relativistic Slater-Dirac wave functions for computations of $\triangle f'$ and $\triangle f''$. Such calculations are very elaborate, but they should show good agreement with experimental data.

The results of these calculations are compared. - For the calculations of dispersion corrections only electron transitions from the discrete into the continuum spectrum have been considered. Transitions into the discrete spectrum are however then of importance, if the energy of the X-rays is very close to the energy of an atomic absorption edge.

Cromer, Don T. & Liberman, D. (1970). J.Chem.Phys. 53, 1891
Hönl, H. (1933). Ann.Physik 18, 625
Parratt, L.G. & Hempstead, C.F. (1954). Phys.Rev. 94, 1593

THE SIGN $\Delta f''$ ACCORDING TO CLASSICAL, SEMICLASSICAL AND QUANTUM FIELD CALCULATIONS.

M.P. Groenewege, Algemene Chemie (afd. Mol.Spectroscopie)
Transitorium III, Uthof, Padualaan 8, Utrecht, The Netherlands.

(Abstract not yet received)

THE DEPENDENCE OF DISPERSION CORRECTIONS ON THE ANGLE OF SCATTERING

A.C. Hazell, Chemistry Department, University of Århus, Denmark.

The real, $\Delta f'$, and the imaginary, $\Delta f''$, components of the dispersion correction has been calculated for elements Z = 10(Ne) to 98 (Cf) for CrKα, CuKα, and MoKα radiations.

The variation with $\sin\theta/\lambda$ was estimated by multiplying the contributions from each shell, k, by the scattering factor, $\phi_k(s)$ for that shell i.e.

$$\Delta f' = \sum_k \Delta f'_k \, \phi_k(s)$$

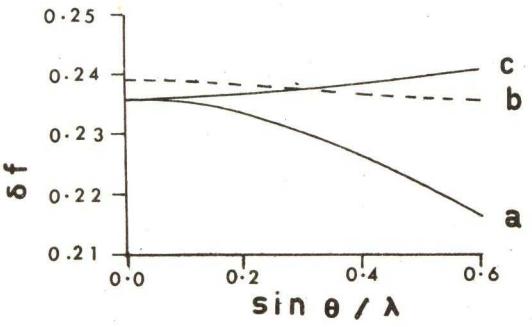
and

$$\Delta f'' = \sum_k \Delta f''_k \phi_k(s)$$

Quadrupole terms and damping were neglected.

The imaginary component always decreases with increasing $\sin\theta/\lambda$. The magnitude of $\Delta f'$ usually varies much less than does $\Delta f''$ since $\Delta f''$ consists only of positive terms whereas $\Delta f'$ usually contains both positive and negative terms and the variations tend to cancel each other. Although the variations are small the effect seems to be greater than that due to the quadrupole terms.

$\delta f = |f| - f_o$ is shown for silicon with CuKα radiation for 3 cases a) dipole terms varying with $\sin\theta/\lambda$, no quadrupole terms.
b) dipole and quadrupole terms both independent of $\sin\theta/\lambda$.
c) dipole terms independent of $\sin\theta/\lambda$, no quadrupole terms.



DISPERSION CORRECTIONS-EXPERIMENTAL DETERMINATIONS

Chairman: S.C. ABRAHAMS

Monday, 14h.00.

DETERMINATION OF DISPERSION CORRECTIONS BY XRAY INTERFEROMETRY

M. Hart
H.H. Wills Physics Laboratory, University of Bristol

Because all of the electrons in an atom scatter in phase in the forward direction there is no error in the theoretical value of the zero order scattering amplitude at zero wavelength.

At other wavelengths, there are considerable difficulties in measuring the real part of the scattering amplitude $\Delta f'$ because of the strong influence of absorption. Interferometric measurements permit a complete separation of the real and imaginary parts of the scattering amplitude, an advantage which is not shared by any other method. Previous measurements by Bonse and Hellkötter (1969), Creagh and Hart (1970) and by Bonse and Materlik (1972) do not exploit the full potential of the xray interferometer and are not suitable for use at those wavelengths which are not available as characteristic lines.

A new mode of operation which has none of these disadvantages and which permits more accurate measurements of $Z + \Delta f'$ at <u>any</u> wavelength will be described. At the conference it is hoped that results for silicon will be presented.

Bonse, U. and Hellkötter, H. (1969) Z. Phys. <u>223</u>, 345-52

Creagh, D.C. and Hart, M. (1970) Phys.stat.sol. <u>37</u>, 753-8

Bonse, U. and Materlik, G. (1972) Z. Phys. <u>253</u>, 232-9

THE DETERMINATION OF HÖNL'S CORRECTIONS FOR COPPER USING A PERFECT CRYSTAL AND CONTINUOUS X-RAYS

Andreas Freund
Institut Max von Laue-Paul Langevin
B.P. 156, F-38042 - Grenoble Cédex, France

Experimental values of Hönl's corrections $\Delta f'$ and $\Delta f''$ for copper will be presented for a wavelength range $0.50 \leqslant \lambda \leqslant 1.66$ Å. Values of $\Delta f''$ have been obtained from absorption measurements whereas $\Delta f'$ has been deduced from the integrated reflecting power of a perfect copper single crystal. Particular attention has been given to the diffraction behaviour in the region near the Cu absorption edge. A double crystal diffractometer and mostly X-rays from the continuous spectrum have been used.

EXPERIMENTAL DETERMINATION OF DISPERSION CORRECTIONS

Professor Ben Post
Physics Department
Polytechnic Institute of New York
Brooklyn, New York 11201

Experimental efforts to determine dispersion corrections fall into two main and partly overlapping categories. One involves efforts to determine x-ray refractive indices; the other involves measurements of atomic scattering factors at frequencies close to those of absorption edges in the atom.

The x-ray refractive indices are determined from, a. deviations from Bragg's Law observed in highly precise measurements of emission line wave lengths, or 'd' values of crystals; b. the critical angle of total external reflections; c. the angular deviations produced by passage of x-rays through prisms; and, d. in recent years, by the phase shift produced in x-ray interferometric measurements when the x-ray beam is passed through the specimen.

The refractive index is related to the atom scattering factor by:

$$n = 1 - \delta = 1 - \frac{\lambda^2 e^2}{2\pi m c^2} \sum_a \left(Z_a + \Delta f'_a \right) N_a .$$

Although δ is in general complex, absorption usually affects measurements of refraction effects to only a minor extent and is generally ignored. The angular deviations due to refraction yield mainly $\Delta f'$, the real part of the dispersion correction.

Measurements of 'absolute' values of atomic scattering have been used extensively, to check on calculated values, and to determine mainly the real parts of dispersion corrections.

'Bijvoet differences' between $I_{(H)}$ and $I_{(\bar{H})}$ have been used mainly to determine the imaginary parts of dispersion terms.

In general, experimental results thus far have been of only limited usefulness. They do lend some support to the prediction of dispersion theory, but, with the exception of interferometric results, cannot yet be used in place of theoretical values.

THE DETERMINATION OF $\Delta f''$ FOR HEAVY ATOMS

D.W. Engel, Physics Department, University of the O.F.S., Bloemfontein, South Africa.

M. Sturm, Max-Planck-Institut für Eiweiss- und Lederforschung, München, Germany (BRD).

The imaginary anomalous scattering factor $\Delta f''$ of Co has been determined experimentally for Mo Kα radiation. 16 selected Bijvoet intensity pairs were measured on a crystal of a coordination polymer $Co(N_2C_3H_3)_2$. The space-group is $I4_1$ and the unit cell contains 32 formula units. (Sturm, 1971).

The value of the effective $\Delta f''_{eff}$ of Co with respect to the light atoms in the cell was found to be 0.78 ± 0.03. An average value of δ (= $\Delta f''/f$) of 0.0003 was used for the light atoms in the structure to obtain $\Delta f''_{Co}$ = 0.79 ± 0.03. The value appears to be significantly lower than the theoretical value of 0.97 (Cromer & Liberman, 1970).

$\Delta f''$ was determined for Br and Mo Kα radiation by measuring 10 Bijvoet-pairs on a compound with formula $C_{11}H_{10}O_4Br$, space-group P1 and 4 molecules in the unit cell. The values obtained were $\Delta f''_{eff}$ = 2.46 ± 0.12 and $\Delta f''_{Br}$ = 2.47 ± 0.12. This agrees with the theoretical value of 2.46.

The importance of making a correction using a neighbouring reflection is stressed (Engel, 1972).

References.

Cromer, D.T. & Liberman, D. (1970). J. Chem. Phys. 52, 1891.

Engel, D.W. (1972). Acta Cryst. B 28, 1496.

Sturm, M. (1971). Thesis, T.U. München.

ANOMALOUS SCATTERING-NOVEL APPLICATIONS

Chairman: R.L. MÖSSBAUER

Tuesday, 9h.00.

IMPLICATIONS OF NON-KINEMATIC AND INELASTIC SCATTERING OF ELECTRONS FOR STRUCTURE ANALYSIS

J. M. Cowley, Department of Physics, Arizona State University, Tempe, Arizona ,USA

A direct analogue of X-ray anomalous scattering does not exist for the diffraction of electrons by crystals. For individual atoms the atomic scattering factor may be assumed to be complex as a result of inelastic scattering processes although the dependence of the effect on the wavelength is weak. This effect is usually overshadowed by dynamical effects, the failure of the first Born approximation for electron scattering, which make the scattering factors complex in a different way. For crystals, both the inelastic scattering effects and the dynamical scattering effects must be considered as properties of coherently scattering regions of the crystal, and not as associated with individual atoms.

In dynamical scattering involving more than two beams, diffracted beam intensities depend on both the amplitudes and phases of the Fourier coefficients of the crystal potential (the structure amplitudes). Hence, in principle, absolute determinations of phases are possible and direct evidence can be obtained for the presence or absence of a center of symmetry and other symmetry elements. These possibilities have been amply demonstrated in experiments with near-perfect small crystals of materials having a simple known structure using convergent beam diffraction patterns and Kikuchi line patterns, but little application has been made of these techniques in the analysis of unknown structures.

In the structure analysis of crystals using powder patterns or 'oblique texture' arc patterns, corrections for n-beam dynamical scattering must be made. On the basis of the Bethe second approximation some phase information may be derived from a comparison of patterns obtained at different voltages.

The complicated dependences of single crystal diffraction intensities on crystal morphology and orientation prohibit their convenient use for structure analysis but proposals are made for the collection of data under controlled near-kinematical conditions to give valuable structural data.

The most important use of single crystal data may well be for refinement of structures determined with limited resolution (about 3Å) by direct imaging in the electron microscope.

The modification of elastic scattering intensities by the presence of inelastic scattering is detectable and has been measured under special conditions of dynamical scattering but its use for structure analysis purposes seems remote. Intensity measurements of the inelastically scattered electrons have been made for both gases and powders. Interpretation in terms of the nature of the excited states of the molecules or crystals is possible although difficult.

ANOMALOUS DISPERSION EFFECTS IN LARGE CRYSTALS

C.A. Wallace, Marconi-Elliot Avionic Systems, Borehamwood, U. K.

It is well known that the presence of anomalous dispersion effects allows the absolute orientation of crystal specimens to be determined non-destructively. The smallness of the X-ray intensity contrast requires careful design of the experiment to maintain symmetry between the reflections to be compared. A general procedure is outlined for obtaining simultaneous reflections from the same crystal area under symmetrical experimental conditions using either characteristic or continuum radiation. This method is particularly suited to large crystals which are acentric or inhomogeneous in texture or perfection, and to thin epitaxial layers as desposited onto crystal substrates, and has been demonstrated for SiC, GaAs, ZnS, InP, and AlN crystals.

In X-ray diffraction topographs of acentric crystals it is possible to display the presence of inversion twinning non-destructively as shown in Quartz, $BaTiO_3$ and $LiNbO_3$. A further consequence of anomalous dispersion is the ability to distinguish between opposite senses of lattice curvature using the dynamical theory of diffraction contrast. As a result it is possible to identify the sense of the Burgers' vector of a dislocation and to differentiate between precipitates which cause a local contraction or expansion of the host lattice.

A UNIFIED APPROACH TO ANOMALOUS SCATTERING AND SOME NOVEL APPLICATIONS OF THE MULTIPLE WAVE-LENGTH METHOD.

S. Ramaseshan, Materials Science Division,
National Aeronautical Laboratory, Bangalore 560017, India.

This paper consists of three parts. In the first part the phenomenon of resonance scattering (of X-rays, neutrons and electrons) will be discussed from the standpoint of the 'optical theorem'. Some general conclusions based on this result will be presented and the different sign conventions for the structure factor and the scattering amplitudes (in X-ray and neutron anomalous scattering) will be clarified.

In the second part an optical analogue for the violation of Friedel's Law will be presented and the dynamical effects like Bormann effect and extinction in polar crystals will be dealt with.

In the third the multiple wave-length method for structural investigations will be considered. These relate to the solution of the 'phase problem' associated with the elliptic motion of atoms (complex polarization vector) in lattice dynamics, the separation of the static displacements in a binary solid solution, and the evaluation of the individual partial structure factors in a binary liquid or amorphous systems. The contribution of the dispersion terms to the scattered intensity from binary liquid systems will be presented. It is also hoped to present experimental data on amorphous As-Te glasses.

IDENTIFICATION OF ATOMIC ENVIRONMENTS BY ANOMALOUS X-RAY SCATTERING AND OTHER PERTURBATION DIFFRACTION METHODS

By J.F. Duncan, A.G. Freeman and J.H. Johnston,

Chemistry Department, Victoria University
of Wellington, New Zealand.

Anomalous scattering is one method by which the intensities of diffracted X-rays at Bragg Angles may be perturbed by resonance methods. By measuring the extent of perturbation for different reflections the percentage occupancy of different sites in the crystal can be determined even at the 2% level using single crystals or powders. The method is also applicable to liquids and enables the pair correlation functions for specific atoms to be determined independently of the bulk liquid structure. Other methods of perturbing the Rayleigh scattered radiation will be discussed, including Mössbauer resonance. Examples of such methods applied to the structural investigation of minor elements in cordierite, and other mineral structures will be given. The limitations of the method, and its advantages over other X-ray methods will be discussed.

CONTRIBUTIONS TO X-RAY DIFFUSE SCATTERING MEASUREMENTS FROM AN INELASTIC SCATTERING ASSOCIATED WITH ANOMALOUS DISPERSION*

Cullie J. Sparks, Jr.
Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

We observed a kind of inelastic x-ray scattering process that differs from those previously reported. This inelastically scattered radiation comes from a resonance emission and differs from the familiar characteristic fluorescence and the Compton and more recently described Compton-Raman (Das Gupta, 1959; Suzuki, 1970) inelastic scattering. The scattered radiation produced when monochromatic x-rays impinge on several elements ranging from Si to Au in atomic number was energy analyzed with a Si(Li) solid state detector. Scattered x-rays of significant intensity were observed at an energy lower than those associated with Compton scattering. Our measurements show these x-rays to peak in intensity at an energy lower than the incident photon by the binding energy of an inner shell electron, to be isotropic in distribution, (independent of scattering angle) and to increase in intensity as the frequency of the incident radiation approaches an absorption edge. We interpret these scattered x-rays as arising from the resonance process associated with the anomalous dispersion correction to the coherent atomic scattering factor for x-rays. Our observed intensities are fitted well by summing the square of the anomalous dispersion amplitudes for each electron which contributes. Thus the cross section for this anomalous scattering appear to come from second-order perturbation theory [the $(\vec{P}\cdot\vec{A})$ term taken twice], a term previously neglected in inelastic x-ray scattering calculations.

These inelastically scattered x-rays can contribute a significant amount to the measured diffuse intensity when the Hönl correction is large, i.e. when the incident radiation is near an absorption edge. This occurs because the energy resolution of the scintillation and proportional counters commonly used is not sufficient to distinguish between the energy of the elastic or Compton and inelastic anomalous scattering. Intensity measurements of the diffusely distributed thermal diffuse scattering, Compton scattering and Lane monotonic intensity from short-range order experiments are shown to contain measurable contributions from this additional inelastic anomalous scattering process. For example, this inelastic resonance scattering can be as large as the Compton scatter when Cu Kα x-rays are scattered from Ni at 60° 2θ.

Das Gupta, K. (1959). Phy.Rev. Letters 3, 38.
Suzuki, T. (1970). Phys.Soc.Japan 29, 730.

*Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

ABSOLUTE CONFIGURATION AND TENSORIAL PROPERTIES

Chairman: S. HOSOYA

Tuesday, 14h.00.

ABSOLUTE SIGN DETERMINATION OF TENSOR PROPERTIES IN RELATION TO STRUCTURE

S. C. Abrahams
Bell Laboratories, Murray Hill, New Jersey 07974

Many physical properties of crystals are expressible in terms of tensors. Some properties, in crystals lacking inversion centers, have tensor coefficients with characteristic signs that are absolute with respect to the atomic arrangement. Such properties include piezoelectricity, pyroelectricity, ferroelectricity, the linear electrooptic and nonlinear optical effects, and optical activity. Determination of absolute senses of tensor coefficients implies prior determination of the absolute structural configuration, and the subsequent relation of the absolute orientation of a given single crystal to the sign of the coefficients measured on the same crystal. Several methods, all using anomalous X-ray scattering in establishing absolute orientation, will be critically considered together with an assessment of microtechniques for measuring specific tensor coefficients. Absolute sense assignment allows the construction of detailed models, based directly on the atomic and electronic arrangement, to account for the nature of the property. Crystals with extended tetrahedral atomic arrays, as in the cubic zinc-blende or tetragonal chalcopyrite structures, develop a charge on compression along a tetrahedral direction as expected on the basis of ionic charge displacement, for the highly ionic case: for the more covalent case, charge transfer must also be included. Polar crystals containing octahedral atomic arrays, as in the perovskite, tungsten-bronze and lithium niobate type structures, generally contain shorter, less-compressive and longer, more-compressive metal-oxygen bonds: the longitudinal piezoelectric coefficient in these crystals has the sign predicted on the basis of resulting ionic charge displacements. The sense of the polarization vector in ionic crystals is similarly predictable from the absolute charge arrangement at a given temperature. The sign of the linear electrooptic or Pockels effect, the change in refractive properties induced by an electric field, is not yet generally predictable. In contrast, the sign of the nonlinear optical or second harmonic generation coefficients is shown to depend (Levine, B. F. (1973), Phys. Rev. B7, 2600) on bond ionicity, d-electron contributions and absolute atomic arrangement. The absolute sense of optical gyration tensor coefficients as a function of structural handedness is briefly considered.

"FERROELECTRIC X-RAY ANOMALOUS SCATTERING EFFECT" APPLIED TO PROBING TRIDIMENSIONAL DOMAINS IN FERRO - ELECTRICS.

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and

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Consider a ferroelectric crystal undergoing an X-ray scattering experiment which is defined by its diffusion vector H. Let I^+ be the scattered intensity when the ferroelectric polarization is parallel to H, and I^- when the polarization is antiparallel to H. Suppose that the crystal is centrosymetrical in its paraelectric phase. Then reversing the polarization is equivalent to transforming H to -H. Because of anomalous scattering there may occur a difference between $I(+H) = I^+$ and $I(-H) = I^-$.

This phenomena, which we have called "ferroelectric X-ray anomalous scattering effect" is shown to be an efficient non destructive method of probing the mean polarization in a 180^o polydomain ferroelectric sample /1/.

When applying this method to $YMnO_3$ we observe relative intensities differences

$$2.\frac{I^+ - I^-}{I^+ + I^-}$$

as high as 70%. This is used in the study of inhomogeneous domain distribution along the thickness of a $YMnO_3$ single crystal plate, which occurs during switching in different regimes.

/1/ Bertaut, E.F. and Lissalde, F (1967). Solid State Comm., 5, 173.
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Lissalde, F and Peuzin, J.C. (1972). Ferroelec. 4, 159.

APPLICATION OF ANOMALOUS SCATTERING TO CHIRALITY (INDUCED NONCENTROSYMMETRY)

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Although anomalous dispersion has been used to determine the absolute configuration of about 500 crystal structures, the great majority were undertaken to ascertain the chirality of the molecular units for chemical or biochemical purposes. Its application to crystals where chirality arises solely from the crystal structure has lagged badly and is only recently beginning to be applied in earnest to assist correlation of anisotropic properties with absolute configuration of the structure. It is intended to review what has been achieved; the potential of the method in relation to structures where noncentrosymmetry arises either naturally or in response to various inducing factors; and to consider the sensitivity limits of the technique.

ANOMALOUS DISPERSION AND DIFFRACTION SYMMETRY

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I. Space-group dependent symmetry: According to the conventional space-group formalism, the diffraction group for a given crystal is isomorphic with the point group. For non-centrosymmetric crystals the diffraction symmetry is wave-length dependent. Friedel's law is valid when $\Delta f''/(f+\Delta f')$ is constant for all the constituent atoms. (Note that $\Delta f''=0$ is not a necessary condition for Friedel's law.)

II. Structure-dependent symmetry: In certain cases the diffraction symmetry depends not only on the space group but also on the atomic arrangement in an asymmetric unit.
(a) Pseudosymmetry. The problem of pseudosymmetry is frequently encountered in actual crystal-structure analyses or in the determination of the absolute configuration.
(b) False symmetry (diffraction enhancement of symmetry). The diffraction symmetry may be higher, other than as a result of Friedel's law, than that normally expected from the point group. For example, a triclinic crystal with space group P1 may produce diffraction patterns with exact symmetry 2 or m (2/m if anomalous dispersion effect is negligible) in the entire range of reciprocal space [Ramsdell & Kohn (1951); Sadanaga & Takeda (1968); Iwasaki (1972); Okamoto, Okamoto & Ito (1973); etc.]. Sometimes the symmetry enhancement itself depends upon incident waves: there exists, for example, a structure with space group $P\bar{4}$ for which the diffraction group is 4/mmm only when Friedel's law holds and otherwise $\bar{4}$.
(c) Wave-length independent Friedel's law. Similarly, non-centrosymmetric structures of a certain kind may give centrosymmetric diffraction patterns even with anomalous dispersion [Iwasaki (1974)]. These structures, though hypothetical, may contain two or more kinds of anomalous scatterers, and their absolute structures cannot be determined in principle by the ordinary X-ray absorption-edge techniques.

These unusual diffraction symmetries have been explained by the use of the symmetry of vector set. It is shown that the concept of "modulated structure" is also useful for the qualitative understanding of wave-length independent Friedel's law.

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THE ANOMALOUS DISPERSION EFFECT IN $LiGaO_2$ AT TWO WAVELENGTHS

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The atomic scattering factor is a complex quantity so that in acentric structures $I_{hk\ell}$ is different from $I_{\bar{h}\bar{k}\bar{\ell}}$. In 1965 Zachariasen (1) showed that this effect can be expressed by the dimensionless quantity :

$$X_{hk} = \frac{I_{hk\ell} - I_{\bar{h}\bar{k}\bar{\ell}}}{1/2(I_{hk\ell} + I_{\bar{h}\bar{k}\bar{\ell}})} = \frac{4}{|F|^2 + |\Psi|^2} \sum_{j>k} \sum |F_j||F_k|(\delta_j - \delta_k)\sin(\alpha_k - \alpha_j)$$

where F and Ψ are the structure factors corresponding to f and $\Delta f''$ respectively, $\delta_j = \frac{\Delta f''_j}{f_j}$ and α_j is the phase of F_j. Values of $X_{hk\ell}$ up to 2 can be observed in acentric inorganic structures, even when the wavelength used is much smaller than the nearest critical absorption edge of the scattering elements.

Accurate X-ray intensity measurements taken with a Philips automatic four-circles diffractometer on $LiGaO_2$ at two wavelengths (MoKα and CuKα) show that the $X_{hk\ell}$'s can be used to determine experimentally the $\Delta f''$ values. $LiGaO_2$ is orthorhombic, space group $Pna2_1$ and has an ordered wurtzite-like arrangement.

(1) Zachariasen, W.H. (1965) Acta Cryst. 18, 714.

ANOMALOUS SCATTERING-INTENSITY MEASUREMENTS

Chairman: W. HOPPE

Thursday, 9h.00.

ANOMALOUS SCATTERING MEASUREMENTS AND AMPLITUDE AND PHASE DETERMINATION WITH CONTINUOUS X-RAY RADIATION

Sukeaki Hosoya

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(A) The merits are reported on the study of the present subjects by the use of an SSD (solid-state detector) diffractometer and limitation of this method is also pointed out.

(B) The fact that the intensity ratio between any Friedel or Bijvoet pair is independent of the degree of crystal perfection at least in favourable cases was pointed out by Cole et al. (1962) and confirmed by Holloway (1969) and more widely by us. This will be very helpful in some cases in (C) and (D).

(C) The new methods are reported for measuring dispersion curves at any energy region. The crystal preferably has a simple structure where all atoms are at known special positions. Reports are made on the results measured near the GaK absorption edge with an energy step of ca. 1.3eV on GaP and GaAs. The $\Delta f'$ and $\Delta f''$ data obtained are compared with our calculated curves particularly around the K edge. The method varies depending on both whether the absorption coefficient is measured and whether F is real or complex. In the most general case, the two ratios among three measured values of I[h(i),E] with different i's are used.

(D) It is reported that both absolute value of amplitude |F| and its phase angle can be experimentally determined, if the position of an anomalous atom and its dispersion curve are known. The use of the intensity ratios, which can be accurately measured, enables us to extend the idea by Herzenberg et al. (1967) drastically. When F is complex, I[h,E(i)]/I[-h,E(i)] of three pairs can uniquely determine F. Real examples will be shown. In favourable cases, the extinction does not matter because of the fact mentioned in (B). When F is real, the two ratios among three I[h,E(i)] values uniquely determine |F| and its sign, although one ratio may sometimes be enough. As E's are different corrections should be made for differences in Lp, absorption and incident beam intensity at different energies. The extension to the case with anomalous atoms of the same kind is possible. We have only to take the geometrical structure factor due to these atoms as a modifying factor for each reflection.

(E) Anomalous atoms can be located, though not yet done, by the difference Patterson map obtained with two energies where $\Delta f'$ has the same value at both sides of the edge. This is an X-ray version of Sikka's idea (1969) proposed for the neutron case.

(F) The preliminary results are reported on the determination of the polarity sense of hemimorphite and on the structure determination of tetragonal $BaTiO_3$ by the use of the intensity ratios.

Cole, H. & Stemple, N. R. (1962) J. Appl. Phys. 33, 2227-2233.
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ACCURATE MEASUREMENT OF X-RAY INTENSITIES AND BIJVOET DIFFERENCES FROM AN EXTENDED CRYSTAL FACE

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The use of large, flat single crystals which intercept the entire incident X-ray beam in intensity measurements will be described.[1] The advantages and limitations of this method of measurement will be discussed with particular reference to the accurate determination of Bijvoet differences.[2] Results obtained from cadmium selenide whose structural parameters and Bijvoet differences have been measured by this method[3] will be reported. An attempt to determine the dispersion corrections from the measured Bijvoet differences by a least-squares procedure will be described.

[1]Mair, S.L., Prager, P.R., and Barnea, Z. (1971). *J. Appl. Cryst.* 4, 169.

[2]Mair, S.L., Prager, P.R., and Barnea, Z. (1971). *Nature Phys. Sci.* 234, 35.

[3]Freeman, D.K., Mair, S.L., and Barnea, Z., to be published.

INTENSITY MEASUREMENTS

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The purpose of intensity measurements involving anomalous scattering in conjunction with a structure determination is generally twofold; (a) one needs accurate data to obtain a well refined structure, which in turn permits an accurate calculation of anomalous scattering effects; (b) the data must be sufficiently precise to permit a meaningful comparison of observed and calculated anomalous scattering effects.

Although there are many reported cases of successful absolute configuration determinations based data of relatively low accuracy (R in the range 7-15%) caution is always in place. I have in my laboratory an example of an incorrect chirality determination at R~8%. It is well to bear in mind that the overall quality of a study depends critically on the quality of the data.

A number of factors determine precision and accuracy. The most commonly encountered problem areas are associated with the following: (1) counting statistics, (2) radiation damage, (3) apparatus, including crystal support, (4) absorption, (5) scan ranges and accuracy of setting angles, (6) wavelength definition when a crystal monochromator is used.

The single most important factor seems to be (1). Empirically I have found that for Cu radiation light atom crystals containing about 5.10^{18} electrons have given the most satisfactory results; in any case it is highly desirable that at least 80% of the reflections within the Cu sphere obey $I_{net}/\sigma(I_{net}) \geq 3$.

(2) often presents a difficult problem, especially at room temperature where no satisfactory solution exits. Protection against the atmosphere and shielding from unwanted radiation may be helpful. However, in our experience with liq. N_2 data collection (about 10 data sets) we have not experienced a trace of a decay problem, even with compounds of extremely short lifetimes at room temperature. This, together with the many other advantages of low temperature data for organic crystals strongly suggests that this technique be incorporated among standard procedures.

The significance of (3) seems self-evident, yet it happens all too commonly that insufficient attention is given to appropriate electronic upkeep and mechanical adjustments.

In connection with (5) it should be pointed out that the thermal diffuse scattering (TDS) by organic crystals can be strongly anisotropic; the TDS intensity included with the Bragg peak may vary with rotation about the scattering vector so as to yield large differences in net intensity if TDS corrections are not applied.

The geometry commonly used with monochromators leads to the inclusion of wavelengths other than that nominally selected. For MoKα the range typically can be ± 0.015Å. A $NaHF_2$ data set (R=1.2%) was collected with this effect taken into consideration. Data obtained and treated identically, except for consideration of this effect, could be refined only to R=1.6%.

Experiments designed to yield data virtually free of model error influences will also be described. These involve structure refinement with low temperature, high order data and precise measurements of Bijvoet pairs which are to be used for experimental determination of $\Delta f''$ values.

†Financial support from the National Science Foundation is acknowledged.

ANOMALOUS SCATTERING AND ACCURACY OF INTENSITIES

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Groningen, The Netherlands.

Abstract will be available at the Conference.

REFINEMENT PROCEDURES AND ERRORS IN ATOMIC PARAMETERS

Chairman: G. KARTHA

Thursday, 14h.00.

NEGLECT OF DISPERSION AND APPARENT ATOMIC PARAMETERS

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University of Birmingham, Birmingham, U.K.

With modern computing facilities all that needs to be said is 'Do the right calculation and get the right answer'. Dispersion, anomalous or otherwise, cannot affect the real atomic parameters, which are fixed by symmetry, interatomic forces, temperature, etc. Incorrect collection or treatment of the experimental data can, however, lead to incorrect apparent values. Use of only part of the reflexions within the limiting sphere may give incorrect positional parameters (see, e.g., Ueki, Zalkin and Templeton, 1966). Incorrect allowance for atomic scattering factors leads to incorrect temperature parameters (see, e.g., Cruickshank and McDonald, 1967; Gilli and Cruickshank, 1972, 1973; Wilson, 1972). The correct electron density expressions are complex, and existing computer programs may behave in unexpected ways (Sudarsanan, Wilson and Young, 1971; Rogers, Quick and Mazhar-Ul-Haque, 1974). Past difficulties are reviewed, and suggestions are made for the best real approximations to be used if, for any reason, calculations with complex atomic scattering factors are impracticable.

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ANOMALOUS DISPERSION EFFECTS ON ΔF SYNTHESIS AND LEAST-SQUARES REFINEMENT OF CENTROSYMMETRIC STRUCTURES

By G. Gilli

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and A. Del Pra

Istituto di Chimica Organica, Università di Padova, Italia

The neglect of the Δf' and Δf" terms in centrosymmetric structures causes errors whose origin and nature can be easily understood by analysing the corresponding electron density maps.

If Δf' is neglected in the calculation of F_c, the ΔF synthesis contains spurious peaks in the positions of the anomalous scatterers and having the same sign as Δf'. These peaks are surrounded by spherical ripples with a period 1/s (s= radius of the limiting sphere).

On the other hand, if Δf" is neglected in the calculation of F_c, the ΔF synthesis shows positive peaks (surrounded by ripples with period 1/s) in the positions of the anomalous scatterers as well as similar negative peaks in the positions of the non-anomalous scatterers; such peaks can be explained in terms of deconvolution of the Patterson synthesis.

The small parameter shifts caused by the neglect of Δf' and/or Δf" in the least-squares refinement of suitable two-dimensional structures can be related to the general features of the ΔF maps. The observed shifts in overall scale and vibration parameters are in agreement with simple theoretical calculations.

ERRORS IN VARIOUS PARAMETERS CAUSED BY NEGLECT OF ANOMALOUS DISPERSION EFFECT

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In accurate structure refinement it is important to take into account the anomalous dispersion effects (1-3). The neglect of $\Delta f''$, the imaginary component of the scattering factor, in polar space groups for example, can lead to serious co-ordinate errors (4,5). Whereas the co-ordinate errors are expected only in polar space groups, the errors in the electron density, the temperature factor and the scale factor occur in all space groups. It is shown in this paper that the electron density computed in conventional manner (i.e. neglecting the anomalous dispersion effects) contains spurious peaks in addition to the correct peaks when the anomalous dispersion effects are present in the intensity data. The strength and the location of these peaks have been derived in terms of the strength and the location of the peaks in the correct electron density. Further, small changes from their correct values are expected in the temperature and the scale factors if $\Delta f''$ is neglected in the least-squares refinement. The effect of the neglect of $\Delta f''$ is not completely absorbed in the changes in the temperature and the scale factors, and a small increase in the R-factor results. The expressions are derived for the changes in the temperature-, the scale- and the R-factors. An approximate expression is also given to estimate the difference in the R-factors for the two enantiomporphs of a structure.

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3. Ibers, J. A., and Hamilton, W. C. (1964). Acta Cryst. 17, 781.
4. Ueki, T., Zalkin, A., and Templeton, D. H. (1966). Acta Cryst. 20, 836.
5. Cruickshank, D. W. J. and McDonald, W. S. (1967). Acta Cryst. 23, 9.

THE EFFECT OF ANOMALOUS SCATTERING ON ATOMIC PARAMETERS

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The effects of anomalous dispersion components on atomic parameters and charge distributions are reviewed. In non-centrosymetric polar space groups neglect of $\Delta f''$ leads to coordinate errors as high as 0.05A (T.Ueki et al., (1966) Acta Cryst. 20, 836). In centrosymetric crystals no such errors result, as a first approximation but scale, temperature factors are affected (N.S. McDonald and D.W.J. Cruickshank (1967), Acta Cryst. 22, 48; G.Gilli and D.W.J. Cruickshank (1973), Acta Cryst. B29, 1983). Neglect of $\Delta f'$ increases isotropic thermal parameter of the anomalous scatterers when $\Delta f' < 0$ and vice versa if $\Delta f' > 0$. A reverse effect is noticed for the light atoms. Also in general the effects of $\Delta f'$ and $\Delta f''$ tend to oppose each other. In Lithium fluoride experimental Debye-Waller factors and their ratio for lithium and fluorine ions are strongly dependent on $\Delta f'$ corrections used. A change of $\Delta f'$ of F^- from 0.081 to 0.18 (for CuKα) changes the ratio of B^+/B^- from 1.55 to 1.24 (M. Linkoaho and M. Marisalo, (1970), Acta Cryst. A26, 571).

The possible use of ρ_I ($\frac{\sin\theta}{\lambda}$) function for determination of $\Delta f''$ values is pointed out (R. Srinivasan and K.K. Chacko (1967), Curr. Sci. (India) 36, 279; K.K. Chacko and R. Srinivasan (1970), Z. Kristallogr. 131, 88). Also conversely if accurate $\Delta f''$ values are known theoretically, a higher degree of accuracy in atomic coordinates and thermal parameters appears possible.

Features of residual densities in electron distribution are affected even in centrosymetric crystals if dispersion components are neglected (S. Parthasarathy et al. (1970) Z. Kristallogr. 131, 443; A.Del Pra et al. (1972) Acta Cryst. A28, 65).

The possible use of accurate Bijvoet difference data for (a) estimating small deviations in atomic coordinates of an approximately centrosymetric structure from a centrosymetric model (R. Srinivasan et al. (1973), Acta Cryst. in Press) and (b) estimating partial charge (R. Srinivasan and S.S. Rajan, unpublished) on atoms in simple structures is pointed out.

USE OF ANOMALOUS DISPERSION EFFECTS IN THE SOLUTION OF STRUCTURES

by

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England

Measurements of diffraction intensities taken at three different wavelengths from a compound crystal can be used to calculate, for each spectrum, the intensity contribution of one of the component atoms if the wavelengths are chosen to be in the neighbourhood of an absorption edge for that type of atom. Data for the component atom intensities may be used to obtain the structure of these atoms; this substructure may be determined either by Patterson methods or by sign - determining methods, and an example of the use of each is described. It is then possible, from the calculated phases for this substructure and from the data at three wavelengths, to compute phases of all the spectra and hence to solve the complete structure. This technique has been applied to determine the structure of $Fe\,Al_2$ (Corby R. N. and Black P. J. Acta Cryst. (1973), B 29, 2669-77). and its application to the structure of another compound (α-Fe Al Si), which is hexagonal with 23 atoms in the asymmetric unit, is described. The effects of systematic errors of scaling and of absorption are discussed.

ACCURATE INTENSITY MEASUREMENTS INCLUDING ANOMALOUS SCATTERING

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(Abstract not yet received)

ANOMALOUS SCATTERING AND THE STRUCTURE ANALYSIS OF MACROMOLECULES

Chairman: A.J.C. WILSON

Friday, 9h.00.

THE APPLICATION OF ANOMALOUS DISPERSION METHODS TO THE STRUCTURE ANALYSIS OF MACROMOLECULAR CRYSTALS

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The determination of atomic position coordinates by means of diffraction techniques relies in principle on a knowledge of the amplitudes and phases of the scattered waves for a sufficiently large number of Bragg reflections. For small unit cells a limited number of intensity measurements often suffices for a determination of the atomic position coordinates. Large unit cells, however, which are typical for macromolecular crystals, such as crystallized proteins, require an experimental determination of both the intensities and the phases of a large number of Bragg-scattered waves. The paper examines the possibilities of measuring such phases by means of resonant scattering of X-rays, neutrons and gamma-rays. The potential use of the method of recoilless nuclear resonant absorption of gamma-radiation, which encounters severe intensity problems, is dealt with in some detail. In this context a discussion will be made of the production of radioactive sources with high luminances, of the cooling problem of the single crystals and of the use of energy and position sensitive area detectors.

THE USES AND LIMITATIONS OF ANOMALOUS DISPERSION DATA FROM PROTEIN CRYSTALS

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All protein crystal structures so far solved have used the technique of isomorphous replacement where heavy atoms are added to the protein crystal, and a geometric construction using the magnitudes of F_p, F_{pH1}, F_{H1}, α_{H1}, F_{pH2}, F_{H2}, α_{H2}, etc., can determine the value of α_p with only one degree of uncertainty, that of hand. The heavy atoms used often show considerable anomalous scattering, and differences can be observed between $F_{pH(+)}$ and $F_{pH(-)}$. However, for many reflections the expected anomalous difference is less than the observed scatter of repeated measurements of $F_{pH(+)}$ or $F_{pH(-)}$.

Measurement of this anomalous data can be used in two ways.

1. The values of $F_{pH(+)}$ and $F_{pH(-)}$, $F_{H(+)}$ and $F_{H(-)}$ can be used directly to help resolve the α_p, or better in a modified technique described by North (North(1965)). Two sets of anomalous measurements will also give the correct hand of the protein structure.

2. Formally the knowledge of F_p, $F_{pH(+)}$ $F_{pH(-)}$ should almost define the value of F_H. It is important to know this to refine heavy atoms accurately for the isomorphous replacement method:
The equations are:-

$$F^2H = F_p^2 + F_{pH}^2 + 2F_pF_{pH} \cdot \cos(\alpha_{pH} - \alpha_p)$$

$$= F_p^2 + F_{pH}^2 \mp 2F_pF_{pH} \sqrt{1 - \left({}^{f}/_{f''}{}^{\Delta}/_{2F_p}\right)^2} \qquad \text{(Singh et al.)}$$

$$\approx \Delta^2\text{ISOM} + ({}^{f}/_{f''}\,\Delta\,\text{ANOM})^2 \qquad \text{(Kartha)}$$

The errors in the data have different effects on these two purposes The observed ΔANOM can reasonably be assumed to be described as true ΔANOM $\pm \Sigma$ where the error is symetrically distributed about zero. The phasing uses ΔANOM so the errors can be regarded as serious but random.

But the estimate of F_H uses

OBS Δ^2ANOM = TRUE Δ^2ANOM + $\Sigma^2 \pm 2\Sigma\Delta$ ANOM

This means the Δ^2ANOM is usually overestimated and therefore F_H^2 is overestimated. Various methods for mitigating this effect will be examined (Vijayan & Dodson (1971), Matthews (1966B)).

Abbreviations used

F_p	-	protein structure amplitude	α_H	-	heavy atom phase
α_p	-	protein structure phase	$F(+)$		$\lvert F_{(hkl)}\rvert$
F_{pH}	-	protein plus heavy atom amplitude or heavy atom derivative amplitude	$F(-)$		$\lvert F_{-h-k-l}\rvert$
			Δ ISOM		$\lvert F_{pH}\rvert - \lvert F_p\rvert$
α_{pH}	-	heavy atom derivative phase	Δ ANOM		$\lvert F_{pH(+)}\rvert - \lvert F_{pH(-)}\rvert$
F_H	-	structure factor due to heavy atoms only			

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THE DETERMINATION OF PHASES OF ERYTHROCRUORIN USING THE TWO WAVELENGTH METHOD WITH IRON AS ANOMALOUS SCATTERER.

Erythrocruorin is a haem protein with a molecular weight of $\sim$ 16.000. Its structure has been determined by R. Huber et al. using the multi-isomorphous replacement method with 8 derivatives. [1] We have undertaken a systematic experimental study with the aim to determine phases using the two wavelength method with the iron atom of the haem group as anomalous scatterer. The radiations used were NiKα and CuKα. It was quite clear that a measurement of the extremely small intensity differences was only possible, if the related measurements could be done on the same crystal. We, therefore, constructed a two wavelength diffractometer. In order to minimize radiation damage and other sources of instability we divided the measuring time of every reflexion into about 10 increments and measured these increments in alternating succession. The measuring time for one phase was of the order of 1 hour. Special methods had to be worked out for the correction of the experimental errors, especially for the correction of absorption. We measured appr. 600 phases with an averaged phase error $\sim 50^{\circ}$ (phase error in Huber's measurement $\sim 30^{\circ}$). For practical work the measuring time in single channel diffractometers is too long; but with multi channel diffractometers this method should be useful even for quite big protein crystals. General conclusions, deducted from these results will be reported in the lecture.

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1) HUBER, R., EPP, O. & FORMANEK, H. (1969). Naturwiss. 56, 362.

USE OF ANOMALOUS SCATTERING IN PROTEIN STRUCTURE ANALYSIS.

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In the structure investigation of macromolecules by single crystal diffraction techniques, the use of direct methods of solving the phase problem has been of very limited applicability so far. The outstanding progress in our understanding of the macromolecular tertiary structures during the last decade has been through the preparation and examination of isomorphous derivative crystals with a few atoms of high atomic numbers bound at specific sites in the molecule. The anomalous scattering properties of these atoms cause measurable differences in the intensities of Friedel pairs of reflections. Accurate measurement of these differences are of great value, not only in locating the heavy atoms in the unit cell but also in establishing and refining the phases of the protein reflections.

Occasionally, situations arise where the native protein itself contains heavy atoms, and in such cases, these atoms could, more or less, be directly located by their anomalous scattering properties. Under ideal conditions, knowledge of these positions along with an accurate set of diffraction data may be sufficient to provide a satisfactory set of initial protein phases for a rough preliminary protein model. Further, these phases could readily be used for screening isomorphous heavy atom derivative crystals. As satisfactory derivative crystal data become available, these phases may be refined by usual methods to improve the electron density model of the protein molecule.

ANOMALOUS SCATTERING AND THE STRUCTURE ANALYSIS OF MACROMOLECULES

STRUCTURE DETERMINATION USING NEUTRON ANOMALOUS SCATTERING

Chairman: A. VOS

Friday, 14h.00.

ANOMALOUS SCATTERING IN PROTEIN STRUCTURE ANALYSIS

By

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The theory of anomalous scattering in determining phases of protein reflections was developed by Blow and Rossmann (Acta Cryst. (1961), 14, 1195), and applied in the structure analysis of lysozyme where it was found to have had a marginal effect in determining the centroids of the probability distributions (North, Acta Cryst. (1965), 18, 212). Anomalous scattering data were used in solving the structure of extracellular nuclease with multiple derivatives (Arnone et al., J. Biol. Chem. (1970), 241, 4389). Both rubredoxin and ferredoxin, however, were initially solved by the single isomorphous derivative method and anomalous scattering measurements were used to resolve the phase ambiguity (Herriott et al., J. Mol. Biol. (1970), 50, 391; Sieker et al., Nature (1972), 235, 40).

Flavodoxin from D. vulgaris provides a good test of the power of anomalous scattering in determining the phases in protein crystallography. Crystals of the protein are tetragonal, space group $P4_32_12$, unit cell dimensions a = 51.6 Å, c = 139.6 Å. About 60% of the crystal volume is solution. The structure was solved at 2.5 Å resolution (Watenpaugh et al., Proc. Nat. Acad. Sci. (1972), 69, 3185) and extended to 2 Å resolution with phases derived from a single-site Sm^{3+} derivative. The quality of the 2.5 Å map was sufficient to trace the polypeptide chain throughout the molecule and the FMN could easily be distinguished. At 2 Å resolution most side groups can be identified. Along with the sequence information, the 2 Å resolution electron density map is being used to derive coordinates for all atoms in the molecule. The large amount of solvent in the crystals forms a three-dimensional system of interpenetrating channels 20-30 Å wide extending throughout the structure. Even in channels of this size there appears to be considerable structure in the solution.

ANOMALOUS SCATTERING IN PROTEIN STRUCTURE ANALYSIS

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The importance of anomalous scattering with phase shift in crystal structure analysis arises due to its ability to obtain the absolute configuration and to determine the phases of reflections of non-centrosymmetric crystals. The successful application of this method for structure determination depends largely on the possibility of measuring fairly accurately the Bijvoet differences of a large percentage of reflections. The optimum conditions for the measurability of Bijvoet differences will therefore be examined first from statistical distribution of the Bijvoet difference and the Bijvoet ratio. The use of the measured Bijvoet differences for the location and correlation of the positions of the replaceable atoms in different derivative crystals to a common origin, its use for obtaining the phase probability distribution via the Blow and Crick criterion and the methods of combining the anomalous scattering and isomorphous data at the various stages of structure determination will be described. The possibility of using the quasi-anomalous and weighted anomalous syntheses for structure determination will also be considered.

USE OF ANOMALOUS SCATTERING IN STRUCTURE SOLUTION

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NEUTRON ANOMALOUS SCATTERING TO PHASE PROTEIN STRUCTURES

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Neutron diffraction studies on proteins (Schoenborn 1969,1971) allow the determination of hydrogen and/or deuterium atoms; atoms that are of prime importance in the structural and catalytic functions of proteins (Blow and Steitz 1970). The heavy atom type isomorphous phasing common in protein x-ray crystallography is however not possible in neutron diffraction. The large anomalous dispersion of certain isotopes enables however the phasing of neutron diffraction data.

Cd^{113}, Sm^{149}, Gd^{155} and Gd^{157} are particularly good candidates; these isotopes are stable, have resonances in a suitable wavelength region and can be bound to proteins, particularly to Ca binding proteins. Anomalous derivatives of met myoglobin (MW 17,000) were crystallized containing either Cd^{113} from cadmium acetate or Gd^{157} from Gadolinium triiodide. Initially, a total of over 5000 reflections were measured for the Cd derivative at .8 Å and 1.25 Å. This data reduced to about 1000 independent Miller pairs for each wavelength. Since the anomalous differences are only a few percent of F, reflections with an error of more than 2% had to be discarded reducing the data set further.

The anomalous dispersion "site" was determined by difference (ΔF^2) Patterson maps yielding one anomalous binding site with x = .43 and z = .61. An x-ray difference Fourier analysis corroborated these results and fixed the y coordinate to .29 to agree with the origin of the Kendrew structure. A least square refinement of the neutron data gave an occupancy factor of .8. Phases from these data were calculated by a treatment basically similar to the x-ray case as described by North (1965) and Matthews (1966). Cd is not the best anomalous disperser for proteins since its resonance lies at .68 Å, making it impossible to collect data on either side of the resonance peak. Protein data collection even at .8 Å is difficult, neutron flux is low and the reflections are barely separated resulting in inaccurate background determination with a resultant large error. Gd^{157}, Gd^{155} and Sm^{149} are better suited but so far no single site, high occupancy myoglobin derivative could be found. Present trials with various Gadolinium compounds yielded some single and double but low occupancy sites considered not yet suitable for anomalous phasing.

The results obtained with Cd-Mb show that phasing of neutron protein data is quite feasible especially with the advent of novel large two dimensional neutron counters that are now being developed for this purpose in this laboratory. (Research supported by the U. S. Atomic Energy Commission.)

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NEUTRON DIFFRACTION STUDY OF $NaSmEDTA \cdot 8H_2O$: AN EVALUATION OF METHODS OF PHASE DETERMINATION BASED ON THREE-WAVELENGTH ANOMALOUS DISPERSION DATA*

by Thomas F. Koetzle and Walter C. Hamilton,† Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

The complex salt $NaSmEDTA \cdot 8H_2O$ is isomorphous with several related lanthanide EDTA complexes which have been studied by x-ray diffraction techniques (Hoard et al., 1965). Crystals of the samarium complex (Space Group Fdd2, a = 19.47(2), b = 35.57(3), c = 12.13(1) Å, Z = 16) were grown using naturally occurring samarium containing 13.8 percent of the resonant isotope ^{149}Sm. Neutron anomalous dispersion data were collected at three wavelengths (λ_1 = 0.83, λ_2 = 1.04, and λ_3 = 1.24 Å) in the vicinity of the ^{149}Sm (n,γ) resonance at 0.92 Å. Intensities were measured for 119 Bijvoet pairs hkℓ and hk$\bar{\ell}$ and for 29 reflections in the centric hk0 zone having $d^* < 0.5$ Å^{-1}. Complete anomalous data (4200 reflections) out to $d^* = 1.0$ Å^{-1} were also collected at λ_3.

Samarium scattering lengths of $b(\lambda_1) = 0.7+0.6i$, $b(\lambda_2) = -0.1+0.6i$, and $b(\lambda_3) = -0.1+0.3i$ were calculated with a single-level Breit-Wigner formula. The samarium ion was located in an anomalous difference Patterson map computed with $\overline{F^2}(\lambda_2)-\overline{F^2}(\lambda_3)$ as coefficients, where $\overline{F^2} = [F^2(hk\ell) + F^2(hk\bar{\ell})]/2$, and the samarium coordinates were refined on the basis of these difference F^2 values. The position of the samarium ion agreed with that found for the lanthanum ion in $KLaEDTA \cdot 8H_2O$. Using the λ_1 and λ_3 data, phases were calculated for the reflections with $d^* < 0.5$ Å^{-1} by the analytical method of Singh and Ramaseshan (1968). These calculated phases will be compared with phases obtained from least-squares refinements of the structure based on the complete λ_3 data in an attempt to assess the utility of the three-wavelength method of phase determination.

*Research performed under the auspices of the U.S. Atomic Energy Commission. An earlier account of this work was presented at the Albuquerque, N.M. A.C.A. Meeting (1972), Abstract 07.

†Deceased.

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APPLICATION OF NEUTRON ANOMALOUS DISPERSION IN THE STRUCTURE DETERMINATION OF CADMIUM TARTRATE PENTAHYDRATE.

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Neutron anomalous scattering has been used to solve the phase problem for the structure of cadmium tartrate pentahydrate $CdC_4H_4O_6\ 5H_2O$. The crystal belongs to the space group $p2_1$ with $a = 6.129$, $b = 12.314$, $c = 7.672$ Å and $\beta = 116^{\circ}14'$. The neutron intensities of Bijvoet pairs upto $\sin\theta/\lambda = 0.45$ Å^{-1} have been measured at $\lambda = 1.03$Å. The average Bijvoet ratio for the observed reflections is 0.18. To locate the Cd atom, a Patterson synthesis with coefficients $(|F(hkl)| - |F(\bar{h}kl)|)^2$ was computed. The highest peak in its (U,0.5,W) Harker section was assigned to the Cd - Cd vector. Using the coordinates of the Cd atom, the two possible phase angles for each reflection were calculated according to the method of Ramachandran and Raman (Current Sci. (1956) 11, 348). From the Fourier map calculated using both the phases, two water oxygens and 5 atoms of the tartrate molecule were picked. Rest of the structure was then obtained by usual methods. A comparison of the above procedure was also made with the Sine Patterson method (Pepinsky and Okaya, Proc. Nat. Acad. Sci. (1956) 42, 286), which was interpreted with the help of Burger's minimum function technique. The successful solution of this hitherto unknown structure by employing the anomalous neutron scattering from the Cd atom confirms conclusions from earlier studies (e.g Ramaseshan, Current Sci. (1966) 35, 87 and MacDonald and Sikka, Acta Cryst. (1969) B25, 1804) that this technique is a very viable one.

A theoretical analysis of the Bijvoet ratio for neutron Bragg reflections has also been made. It has been found that with proper choice of the incident neutron beam wavelength and concentration of the resonant isotopes (Cd^{113} and Sm^{149}), large $\langle|\Delta I|/I\rangle$ can be experimentally achieved even for complex crystals like proteins.

INFLUENCE OF CRYSTAL LATTICE ON MULTIPLE SCATTERING OF ELECTRONS*

I.A. Tsekhanovskii and S.A. Vorobiev

Nuclear Physics Research Institute of the Tomsk Polytechnical Institute

In the present experiment the intensity distributions of the electrons from a (^{90}Sr-^{90}Y) radioactive source behind the 8 μm $\langle 111 \rangle$ Si single crystal were measured. The angular divergence of the incident beam was about 0.1°. The photograpic records showed the radial "deficit" streaks, surrounded on each side by the enhanced intensity. By changing the crystal orientation relative to the incident beam direction the "star patterns" are removed at the same angle relative to the Gaussian distribution of the multiply scattered electrons. The similar behaviour of the transmitted intensity distribution can be observed for the proton channeling (Chadderton,1966) and for the Kikuchi patterns in the electron diffraction (Hirsch,Howie, Nicholson,Pashley & Whelan,1965).

When the incident beam was aligned in the $\langle 111 \rangle$ direction of a Si crystal the angular distribution of the transmitted electrons was rather narrow. This phenomenon may be caused by the effect of the anomalous transmission of the electron beam, that is observed as a six simmetric spots with the strong intensity at the cross points of low indexed planar streaks around the axial dip. In (Fujimoto,Takago,Komaki,Koike & Uchida, 1972) the phenomena of anomalous transmission was related to the Borman effect.

For large angles of a crystal axis to the incident beam an arch like intensity distribution centered around the axial direction is observed. This phenomenon is related to the correlate scattering of the electrons with the conservation of the total transverse energy (Kumm,Bell,Sizmann,Kreiner & Harder,1972). At the angle of incidence about 3° there appear the "excess" radial streaks with the enhanced intensity of the electrons in the wide-angle scattering region.

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