equations corresponding to (7) for the three-beam case can be given as follows:

$$I_{\mathbf{h}} = (I_0 - I_{op1} - I_{op2}) r_{\mathbf{h}} N_{\mathbf{h}} \qquad (A.1a)$$

$$I_{op1} = (I_0 - I_{\mathbf{h}} - I_{op2}) r_{op1} N_{op1} \qquad (A.1b)$$

$$I_{op2} = (I_0 - I_{\mathbf{h}} - I_{op1}) r_{op2} N_{op2}, \qquad (A.1c)$$

where the quantities with the additional suffixes 1 and 2 correspond to $\mathbf{h}_{op1}$ and $\mathbf{h}_{op2}$, respectively. After (*A*.1) has been solved, the intensity escaping from **h** to $\mathbf{h}_{op1}$ and $\mathbf{h}_{op2}$ *via* relevant cooperative points can be written as $(r_{co1}N_{co1} + r_{co2}N_{co2})I_{\mathbf{h}}$; with that coming to **h** from $\mathbf{h}_{op1}$ and $\mathbf{h}_{op2}$ as $(r_{co1}N_{co1}I_{op1} + r_{co2}N_{co2}I_{op2})$. Following the discussion in § 2.2, and neglecting the terms of third and fourth order in r, we find the relation corresponding to (10) as follows:

$$\begin{aligned}(I_h)_{obs}/I_0 \simeq\ & rN_{\mathbf{h}}\{1 - r(N_{op1} + N_{op2})\} \\ & - r^2 N_{\mathbf{h}}(N_{co1} + N_{co2}) \\ & + r^2(N_{op1}N_{co1} + N_{op2}N_{co2}). \qquad (A.2)\end{aligned}$$

Comparing this equation with (10), and extending the discussion to the case of the existence of three or more operative points, we find that the effect of the n-beam interaction can be described by summing up the effects of independent three-beam interactions arising from pairs of h and individual operative points, provided that r is still small for third and further diffractions.

APPENDIX *B*

The polarization factor for three-beam cases is described in the following. The quantity ρ given by Zachariasen (1965) can be expressed as

$$\tan \rho = \tan \chi \sin (\phi + 2\theta), \qquad (B.1)$$

where χ and ϕ are the angles made by the projection of I_{op} on to the $I_0 I_{\mathbf{h}}$ plane with I_{op} and I_0, respectively (Fig. 1). According to Azaroff (1955),

$$\begin{aligned}p_{co} = \{ & (\cos^2 \beta \cos^2 \rho + \sin^2 \rho) \cos^2 \alpha \\ & + \cos^2 \beta \sin^2 \rho + \cos^2 \rho\}/(1 + \cos^2 \beta), \qquad (B.2)\end{aligned}$$

where α and β are the angles made by I_{op} with $I_{\mathbf{h}}$ and I_0 respectively. p^*_{co} will be obtained by replacing β by 2θ. The total p factors are consequently $p_{\mathbf{h}}p^*_{co}$ and $p_{op}p_{co}$ for *Aufhellung* and *Umweganregung*, respectively.

References

AZAROFF, L. V. (1955). *Acta Cryst.* **8**, 701-704.
CHANG, S. L. & POST, B. (1975). *Acta Cryst.* **A31**, 832-835.
COPPENS, P. (1968). *Acta Cryst.* **A24**, 253-257.
LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*, p. 32. New York: Cornell Univ. Press.
MATSUMOTO, T. (1983). *Kōbutsu-gaku Zasshi* (*J. Miner. Soc. Jpn*), **16**, 99-108 (in Japanese).
MOON, R. M. & SHULL, C. G. (1964). *Acta Cryst.* **17**, 805-812.
PANKE, D. & WÖLFEL, E. (1968). *J. Appl. Cryst.* **1**, 255-257.
POST, B. (1975). *Acta Cryst.* **8**, 452-456.
RENNINGER, M. (1937). *Z. Phys.* **106**, 141-176.
SAMUELSON, E. J. (1974). *J. Phys. C*, **7**, L115-L117.
SAMUELSON, E. J. & STEINSVOLL, O. (1975). *J. Phys. C*, **8**, L427-L429.
SASAKI, S. & MATSUMOTO, T. (1977). *Proc. Jpn Acad.* **53B**, 84-89.
SASAKI, S., MATSUMOTO, T. & SAWADA, C. (1981). *Phys. Chem. Miner.* **7**, 260-267.
SHIRANE, G., CHIKAZUMI, S., AKIMITSU, J., CHIBA, K., MATSUI, M. & FUJII, Y. (1975). *J. Phys. Soc. Jpn*, **39**, 949-957.
THOMPSON, P. & GRIMES, N. W. (1977). *J. Appl. Cryst.* **10**, 369-371.
ZACHARIASEN, W. H. (1965). *Acta Cryst.* **18**, 705-710.

Acta Cryst. (1985). A**41**, 133-142

Tensor X-ray Optical Properties of the Bromate Ion

BY 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* 6 *July* 1984; *accepted* 17 *September* 1984)

Abstract

Linearly polarized synchrotron radiation has been used to observe X-ray dichroism of the bromate ion near the bromine K edge by transmission absorption spectroscopy using a crystal of potassium bromate, and to measure the anomalous scattering of bromine and its anisotropy in diffraction experiments with sodium bromate. The principal values of f'' are as high as 12 and 17 electrons atom^{-1} and of f' as low as −13 and −15 for polarization respectively parallel and perpendicular to the threefold axis. The anisotropy is as much as 6·6 for f'' and 4·6 for f', or a few percent more after correction for thermal motion and for incomplete polarization of the beam. A consequence of this large anisotropy is that reflections forbidden by the screw-axis rules are observed. Applications and possible adverse consequences of these effects in structure research are discussed. An energy calibration gives 13 482·1 (10) eV or 0·91960 (7) Å for the peak of the first K-edge absorption line in sodium bromate. These results suggest that X-ray optical activity in sodium bromate can be observed most readily near 0·9205 Å, where the magnitude is estimated to be of the order of 0·1° cm^{-1}. Crystal structures were redetermined for $KBrO_3$, $R3m$, $a = 6·011\,(1)$, $c = 8·152\,(2)$ Å, $Z = 3$, 295 K, $R = 0·010$ for 308 unique reflections, and for $NaBrO_3$, $P2_13$, $a = 6·705\,(2)$ Å, $Z = 4$, 296 K, $R = 0·013$ for 433 unique reflections.

1. Introduction

X-ray dichroism, or dependence of absorption spectrum on polarization direction, occurs in many substances for wavelengths near absorption edges and in the EXAFS regions (*e.g.* Heald & Stern, 1977, 1978; Templeton & Templeton, 1980, TT80 for short; Cox & Beaumont, 1980; Kutzler, Scott, Berg, Hodgson, Doniach, Cramer & Chang, 1981). Where there is dichroism there is a birefringence, and complications occur in beam propagation and scattering. One of these complications is anisotropy of anomalous scattering as a function of polarization, a phenomenon that we first demonstrated in experiments with salts of the uranyl ion (Templeton & Templeton, 1982, hereafter TT82).

In the present paper we describe similar experiments with crystals of sodium bromate and potassium bromate at wavelengths near the K absorption edge of bromine. We expected the microscopic optical properties of the bromate ions to be nearly the same in these two salts. The microscopic anisotropy of absorption is observed at the macroscopic scale in a crystal, like potassium bromate, in which all the bromate ions have the same orientation. The sodium salt is more convenient for the diffraction experiments because its cubic symmetry removes some complications of correction for absorption and macroscopic birefringence.

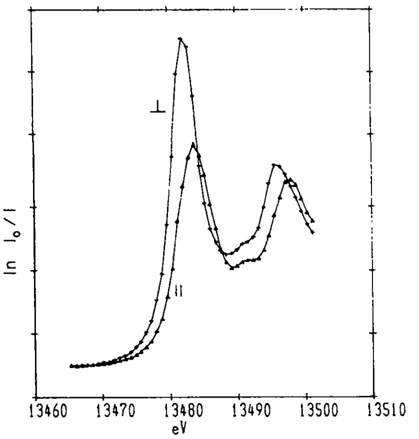

Fig. 1. Polarized X-ray absorption spectra for potassium bromate near the Br K edge.

The anistropy of anomalous scattering found for bromate is considerably greater than that observed for uranium. One result of this fact is that a more complicated analysis of diffraction intensities is required. Another is that reflections forbidden by the screw-axis rule for systematic absences are observed, as predicted by TT80 and discussed in more detail by Dmitrienko (1983, 1984). The effects of thermal motion and of imperfect beam polarization on these results are estimated. Redeterminations of the crystal structures of these two bromate salts, needed for the analysis of these experiments, are reported, as is a calibration of the wavelength scale.

Experiments with synchrotron radiation were carried out at the Stanford Synchrotron Radiation Laboratory (SSRL). The fact that this radiation has strong linear polarization simplifies the observation of the effects discussed here. It should be noted, however, that polarization anisotropy will affect diffraction experiments even when the initial radiation is unpolarized. This anisotropy is not a universal property of the element, but rather is sensitive to chemical state and molecular geometry. The results presented here for the bromate ion have little relation to the properties of bromine in other oxidation states.

2. X-ray dichroism in potassium bromate

Single-crystal polarized absorption spectra (Fig. 1) were measured by transmission technique with a flat crystal of $KBrO_3$, whose largest face was (101). The bromate ion has the shape of a trigonal pyramid, and in the crystal structure of this salt (see below) all the bromate ions have the same orientation. An Enraf-Nonius CAD-4 diffractometer (Phillips, Cerino & Hodgson, 1979) was used to orient the crystal and to measure the transmitted intensity (with the beam stop removed), while an ion chamber in front measured the incident intensity. The c axis (which is parallel to the symmetry axis of each bromate ion) was set horizontal for the 'parallel' spectrum and vertical for the 'perpendicular' spectrum. In each case the beam direction was perpendicular to the c axis and as nearly perpendicular to the largest face as possible. Nearly monochromatic radiation (energy spread *ca* 2 eV) was provided by a double-crystal (Si_{111}) monochromator on beam line II-2 at SSRL. This radiation has a high degree of linear polarization with the predominant electric vector in the horizontal plane.

The degree of polarization of the radiation in these experiments is unknown. It would be 100% in the limit of ideal electron orbits, perfect alignment and zero vertical angular acceptance. But alignment is not perfect, and the orbits are subject to small vertical oscillations. We estimate that the polarization was in the range 90 to 95% in these experiments, based on subsequent measurements (Templeton & Templeton, 1984) using a Borrmann-effect analyzer (Cole, Chambers & Wood, 1961). Polarization is defined as $(I_h - I_v)/(I_h + I_v)$, so that 90% polarized means that the horizontal component is 19 times as intense as the vertical one.

The spectra in Fig. 1 show two strong absorption peaks for each polarization, shifted one or two eV toward lower energy for polarization perpendicular to the threefold axis of the bromate ion. The peak nearest the absorption edge is considerably stronger for perpendicular polarization, and the greatest anisotropy of absorption occurs near its peak.

These spectra are presented without any correction for the imperfect polarization of the beam, and they were calculated in the usual way assuming that attenuation is an exponential function of thickness and absorption cross section. The result is that the anisotropy is underestimated. When the attenuation is small (*i.e.* thin samples or small cross section) the underestimation is by the same factor as the degree of polarization. However, when the attenuation is large the errors can be greater. In these experiments the intensities were reduced by as much as a factor of 300 at the peak absorption. Thus in the perpendicular spectrum the observed counting rate at the peak is mainly due to a small amount of vertically polarized photons because the horizontally polarized ones are almost completely absorbed. The results of diffraction experiments described below indicate that the maximum anisotropy is underestimated by about a factor of two. Such an error is possible if the polarization is about 90%. A rigorous analysis of the present spectra is not possible because of complications of uneven sample thickness and imprecise duplication of geometry for the two sample orientations.

Another possible source of error in estimating the anisotropy is contamination of the beam with harmonic wavelengths, which are highly penetrating and can be important when the radiation of interest is highly absorbed. In the present case the harmonics were minimized by a combination of the choice of monochromator crystal, adjustment of the crystals to be not quite parallel, and pulse-height gating of the scintillation counter signals. As a result of these precautions, harmonic radiation is not believed to contribute significantly to these spectra.

3. Polarized anomalous scattering in sodium bromate

As described by TT82 one can observe the effects of polarization anisotropy of anomalous scattering in diffraction experiments using cubic crystals and at the same time avoid several complications of beam propagation and absorption that would occur if the crystal were less symmetrical. For this reason we chose sodium bromate for these experiments. The macroscopic absorption parameter is free of linear dichroism, and diffraction intensities can be corrected for absorption in the usual manner. Nor need we consider beam splitting due to macroscopic birefringence.

The atomic scattering factor for bromine may have a different value for each combination of polarization directions for incident and scattered rays. The polarization is described in terms of three unit (column) vectors: **s** is perpendicular to the plane that contains the incident and scattered rays, **p** is perpendicular to **s** and to the incident ray and **p**′ is perpendicular to **s** and to the scattered ray. In the dipole approximation the complex scattering factor is given by a matrix product for each of four polarization cases (TT82; Dmitrienko, 1983):

$$f_{ss} = \mathbf{s}^T\mathbf{f}\mathbf{s}$$
$$f_{sp} = \mathbf{s}^T\mathbf{f}\mathbf{p}'$$
$$f_{ps} = \mathbf{p}^T\mathbf{f}\mathbf{s}$$
$$f_{pp} = \mathbf{p}^T\mathbf{f}\mathbf{p}',$$

where the superscript T indicates transpose. In a Cartesian coordinate system with its z axis in the direction of the symmetry axis of the bromate molecule, the scattering factor tensor **f** has the form

$$\mathbf{f} = \begin{pmatrix} f_\pi & 0 & 0 \\ 0 & f_\pi & 0 \\ 0 & 0 & f_\sigma \end{pmatrix}.$$

The principal values of f are

$$f_\pi = f_0 + f'_\pi + if''_\pi$$

for the two directions perpendicular to the symmetry axis and

$$f_\sigma = f_0 + f'_\sigma + if''_\sigma$$

for the symmetry direction. If the incident radiation has perfect **s** polarization, the f_{ps} and f_{pp} terms need not be considered. In the present experiments they are not zero, but they were neglected. For the estimated polarization of 90% or better, the corresponding contributions to measured intensity must be multiplied by a factor of 0·05 or smaller. This factor makes the effect of f_{ps}, which is already a small term, quite negligible. The intensity due to f_{pp} tends to be smaller than that of f_{ss} by a factor $\cos^2 2\theta$, the normal polarization factor; this additional factor makes its effect unimportant in the individual reflection measurements that have large scattering angles. Neglect of this term introduces a bias that causes us to underestimate the anisotropy by a few percent at most. We hope to make a more rigorous treatment of future experiments in which the polarization is measured at the same conditions used for the diffraction experiments.

Table 1. *Anisotropic anomalous scattering of bromine*

Units are electrons atom^{-1} for the f parameters; λ, from the monochromator setting, may be high by *ca* 0·00007 Å; R is the agreement index from least squares with N reflections.

λ(Å)	f'	f'_2	f'_σ	f'_π	f''	f''_2	f''_σ	f''_π	R	N
0·91862	−5·0 (1)	−0·8 (1)	−5·5 (1)	−4·7 (1)	5·51 (9)	−0·9 (1)	4·9 (1)	5·8 (1)	0·042	687
0·91879	−6·0 (2)	−0·7 (2)	−6·5 (2)	−5·8 (2)	5·1 (1)	0·1 (2)	5·2 (2)	5·1 (1)	0·047	362
0·91922	−5·7 (2)	−0·7 (3)	−6·2 (3)	−5·5 (2)	4·1 (2)	−0·6 (3)	3·7 (3)	4·3 (2)	0·078	467
0·91944	−2·4 (1)	−0·9 (2)	−3·0 (2)	−2·1 (1)	4·1 (1)	0·4 (1)	4·4 (1)	4·0 (1)	0·041	432
0·91954	−1·0 (2)	−2·7 (3)	−2·8 (3)	−0·1 (2)	7·2 (2)	0·7 (3)	7·7 (3)	7·0 (2)	0·063	632
0·91957	−1·1 (4)	−3·1 (4)	−3·2 (5)	−0·1 (4)	8·3 (3)	0·3 (3)	8·5 (4)	8·2 (3)	0·074	605
0·91959	−1·4 (2)	−1·9 (2)	−2·7 (2)	−0·8 (2)	6·4 (2)	0·6 (2)	6·8 (2)	6·2 (2)	0·053	705
0·91960	−1·7 (3)	−3·7 (2)	−4·1 (3)	−0·4 (3)	9·2 (3)	−0·3 (2)	9·1 (2)	9·4 (2)	0·074	644
0·91965	−5·6 (4)	−4·6 (3)	−8·7 (4)	−4·1 (3)	13·7 (3)	−3·7 (3)	11·2 (4)	14·9 (3)	0·095	921
0·91971	−9·8 (7)	−1·8 (8)	−11·0 (9)	−9·2 (7)	15·6 (5)	−5·4 (7)	12·0 (7)	17·4 (6)	0·119	317
0·91973	−12·8 (3)	−0·9 (3)	−13·4 (4)	−12·5 (3)	12·5 (3)	−6·6 (3)	8·1 (4)	14·7 (3)	0·102	624
0·91976	−14·50 (8)	2·6 (2)	−12·8 (2)	−15·4 (1)	6·3 (1)	−3·7 (2)	3·8 (2)	7·5 (1)	0·093	627
0·91981	−13·9 (1)	3·1 (3)	−11·8 (2)	−14·9 (1)	4·2 (1)	−1·5 (2)	3·2 (2)	4·7 (1)	0·081	228
0·91987	−12·92 (8)	2·4 (2)	−11·3 (2)	−13·7 (1)	3·25 (7)	−1·1 (2)	2·5 (2)	3·6 (1)	0·077	294
0·92052	−8·21 (5)	0·91 (8)	−7·6 (1)	−8·5 (1)	0·77 (5)	−0·35 (9)	0·5 (1)	0·9 (1)	0·049	370

In our previous analysis of the diffraction data for sodium uranyl acetate (TT82) we also neglected f_{sp}. For sodium bromate neglect of this term is justified for most of the reflections, but for a few of them it is important or even dominant. In particular, reflections forbidden by the systematic-absence rules for the 2_1 screw axes have no contribution from f_{ss}, and f_{sp} is mainly responsible for the intensity. These reflections are quite weak but definitely present. At wavelengths where the anisotropy is large the intensities of 100, 300, 500 and 700 are smaller than the strongest reflections by factors in the range 300 to 1000.

For each reflection one calculates a structure factor F_{ss} that includes sodium and oxygen atoms in the usual way and each bromine atom with a scattering factor f_{ss}. Note that in general f_{ss} has four different values for the four 'equivalent' bromine atoms in the unit cell, because the scattering factor tensor must be rotated to correspond to each molecular orientation. A second structure factor F_{sp}, which includes contributions only from the bromine atoms, uses four values of f_{sp} as the form factors. These two amplitudes of scattered radiation may have coherent phases, but this coherence does not affect the total intensity because the two polarizations are perpendicular. The total intensity is proportional to $G^2 = |F_{ss}|^2 + |F_{sp}|^2$. The most convenient way to adapt our least-squares program for this calculation was to substitute $\Delta = F_o - G$ for $\Delta = F_o - |F_c|$. Appropriate changes were also made in the method of calculation of the derivatives of Δ with respect to the variable parameters.

The synchrotron radiation diffraction experiments were made with two specimens, designated as crystal no. 4 (described in more detail in a later section) and crystal no. 6 (20 faces including all of {111}, eight of {110}, and four of {100}). Beam line II-2 was used without any focusing mirror and with a double Si_{111} monochromator. Diffraction data were taken with the Enraf-Nonius CAD-4 diffractometer in the 'zigzag' mode for reflections in the ranges of θ 4–30, 4–35, 4–49, 14–45 and 30–40° for various sets. In each case each reflection was measured at azimuthal angles $\psi = -20$ and 20°. This was done to make a distinction between the effects of polarization and of possible errors correlated with the diffraction vectors. It also gave protection against multiple-reflection effects. With the highly collimated synchrotron radiation multiple reflections are not very likely because they require very precise setting, but when they occur they can induce very large errors. The number of reflections measured in each set, listed in Table 1, depended on the experimental conditions and the time available. According to cubic symmetry many of the data would be duplications. Because the polarization breaks the symmetry, each reflection (even the same *hkl* at different azimuthal angles) must be treated as an independent datum.

The intensities were normalized according to readings, typically at 10 s intervals, of an ion chamber in front of the diffractometer collimator in order to correct for beam-intensity changes. A standard reflection was measured repeatedly at frequent intervals to verify that the normalization was valid. Sometimes it was not, because the ion chamber was less sensitive than the diffractometer to some kinds of changes of beam alignment. 'Not-equal' checks, in which a forward scan is compared with a reverse scan, were always made, and data that failed the test were rejected. This was a protection against beam changes too brief to be detected by the monitor system. Under the best beam conditions it was rare for a reflection to fail the test, and normalization factors changed slowly and steadily. At other times the beam was less steady, and many reflections were rejected. Reflections were also rejected when too weak for measurement or when strong enough to exceed the linear range of the scintillation counter.

Intensities were corrected for absorption with our analytical absorption program. Correction factors ranged from 1·8 to 170. In order to make the correction it was necessary to estimate the absorption parameter that is related to the f'' values that were being determined. This circularity of the experiment was not very serious because relative values of the absorption corrections are not very sensitive to the parameter μ that is used, and also because there is little correlation between the corrections and the resulting values of f''.

As in TT82, the variables for least-squares refinement were chosen as a scale factor and

$$f' = (f'_\sigma + 2f'_\pi)/3,$$

$$f'_2 = f'_\sigma - f'_\pi,$$

and f'' and f''_2 defined in a similar way. The variables f' and f'' represent the scalar part of the anomalous scattering (the spherical average), and f'_2 and f''_2 describe the anisotropy.

The results of 15 experiments at wavelengths near the K absorption edge are listed in Table 1. The R factors range from 0·041 to 0·119 and are not as good as would be predicted from the nominal statistical accuracy. This disagreement may result in part from approximations of the model used to analyze the data and errors in the absorption corrections. Much of it reflects the instability of the radiation source and the difficulty of preventing small changes in wavelength during the several hours required for each set of measurements. The largest R values occur at wavelengths where some of the parameters change most rapidly with wavelength.

The principal values of f' and f'' are plotted in Fig. 2. For both polarization directions the f'' values at their peaks greatly exceed the maximum of about 4 electrons atom^{-1} calculated from a model, such as that of Cromer & Liberman (1970), which neglects the effects of resonance lines at the edge. The curves of f' both make the large excursions that are characteristic of the effect of a sharp line absorption. In both pairs of curves the perpendicular effects are the more extreme.

The anisotropy terms are plotted in Figs. 3 and 4 and compared with curves derived from the spectra of Fig. 1. For f'' this curve is essentially the difference of the two spectra, with appropriate scaling. The curve for f' is derived by the Kramers–Kronig dispersion relation, with integration confined to the region near the absorption edge where the dichroism is significant. The anisotropy functions derived by the two methods have similar shapes, but the absorption method gives smaller values, for the reasons already discussed.

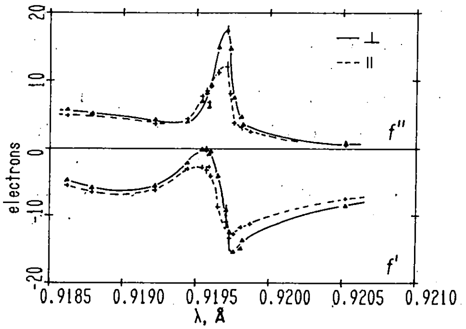

Fig. 2. Principal values of the f' and f'' tensors for Br measured in diffraction experiments with sodium bromate near the K edge.

4. Crystal structure of potassium bromate

Crystals of potassium bromate are rhombohedral with one molecule per primitive unit cell (Zachariasen, 1928). Thus all the bromate ions have the same orientation, each with its threefold axis parallel to the hexagonal c axis, and this substance is suitable for direct observation of the molecular dichroism. A disadvantage is that the crystals are prone to twinning, and it is difficult to find large untwinned crystals. We redetermined the crystal structure to obtain thermal parameters so that we could estimate the effect of molecular libration on the macroscopic dichroism. Incidental to this determination we obtained more precise atomic coordinates than were known before, and also values for anomalous dispersion terms of bromine and potassium for Mo $K\alpha$ radiation.

Crystal data: KBrO$_3$, $M_r = 167\cdot01$, $R3m$, $a = 6\cdot011\,(1)$, $c = 8\cdot152\,(2)$ Å, $V = 255\cdot1\,(1)$ Å^3, $Z = 3$,

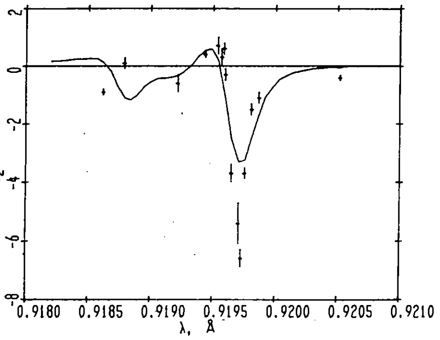

Fig. 3. Anisotropy of f'' from the diffraction experiments (points with error bars) and derived from the difference of the absorption spectra (continuous curve).

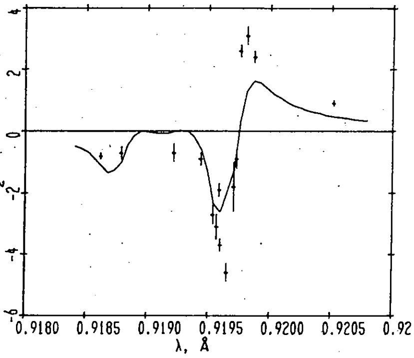

Fig. 4. Anisotropy of f' from the diffraction experiments (points with error bars) and derived with the dispersion integral from the absorption spectra (continuous curve).

Table 2. *Parameters for potassium bromate*

	x	z	B_{11} (Å^2)	B_{33} (Å^2)
Br$^{\mathrm{i}}$	0	0·4827 (3)	1·152 (10)	1·111 (13)
K$^{\mathrm{i}}$	0	0	1·858 (16)	2·69 (9)
O$^{\mathrm{ii}}$	0·14456 (15)	0·4002 (5)	3·18 (5)	2·90 (5)
			[2·27 (5)]*	[0·63 (2)]†

Symmetry code: (i) $0, 0, z$; (ii) $x, -x, z$

* B_{12}; † B_{13}

$D_x = 3{\cdot}261\,(1)$, $D_m = 3{\cdot}27$ g cm^{-3} (*Handbook of Chemistry and Physics*, 1964), Mo $K\alpha$, $\lambda(\alpha_1) = 0{\cdot}70930$ Å, $\mu = 130$ cm^{-1}, $F(000) = 234{\cdot}21$, $T = 295$ K, $R = 0{\cdot}010$ for 308 unique reflections.

Experimental: reagent potassium bromate crystallized from water by slow evaporation. Plate $0{\cdot}04 \times 0{\cdot}07 \times 0{\cdot}15$ mm; CAD-4 diffractometer; cell dimensions from 13 reflections $23 < \theta < 27°$; full sphere to $\theta = 30°$ plus some duplications, and half sphere (h positive) to $\theta = 35°$; three standard reflections, $\sigma = 0{\cdot}009, 0{\cdot}018, 0{\cdot}021$, no correction for decay; 1332 reflections reduced to 308 unique reflections including 152 Bijvoet pairs; $R_{\mathrm{int}} = 0{\cdot}034$; no reflections $< 3\sigma$; refined on F; 15 parameters including f' for Br, f'' for Br and K, and anisotropic thermal parameters for all atoms; $wR = 0{\cdot}012$; $S = 1{\cdot}05$; $w = 1/\sigma^2(F)$, $p = 0{\cdot}015$ in calculation of $\sigma(F^2)$; max. $\Delta/\sigma = 10^{-5}$; max. correction for secondary extinction 8% of F. Atomic scattering factors for neutral Br, K$^+$ and oxygen with charge $-1/3$ (interpolated) were taken from *International Tables for X-ray Crystallography* (1974), as were initial anomalous scattering terms for all atoms. Calculations were made with unpublished local programs. Atomic parameters are listed in Table 2.*

The Br–O bond distance is 1·648 (1) Å uncorrected, or 1·668 Å if corrected for thermal motion by the riding model. The O–Br–O angle is 104·51 (8)°. Each potassium ion has 12 oxygen neighbors, three at 2·923 (3), six at 3·063 (1), and three at 3·593 (4) Å in the configuration described by Gillespie, Gantzel & Trueblood (1962) for ammonium chlorate, which has the same structure.

The principal r.m.s. amplitudes of thermal motion are 0·11, 0·21 and 0·22 Å for the oxygen atom, with minimum amplitude close to the bond direction, and almost isotropic (0·12 Å) for the bromine atom. These values are consistent with nearly isotropic libration with r.m.s. amplitude *ca* 6° about each axis. This libration will tend to decrease the anisotropy of absorption of the crystal relative to that of a static molecule. In the dipole approximation the absorption cross section depends linearly on the square of the cosine of the angle between polarization direction and symmetry axis. If $\sigma_{0\sigma}$ and $\sigma_{0\pi}$ are the principal values of the cross section for the molecule at rest, φ is an angle of libration, and $\langle \sin^2 \varphi \rangle$ is taken as $(\sin 6°)^2 = 0{\cdot}011$, the average cross sections for librating molecules are approximately

$$\sigma_\sigma = 0{\cdot}978\sigma_{0\sigma} + 0{\cdot}022\sigma_{0\pi},$$

$$\sigma_\pi = 0{\cdot}011\sigma_{0\sigma} + 0{\cdot}989\sigma_{0\pi}.$$

Note that rotations about two axes change σ_σ, while only one rotation effects σ_π. The anisotropy

$$\sigma_\sigma - \sigma_\pi = 0{\cdot}967(\sigma_{0\sigma} - \sigma_{0\pi})$$

is thus reduced about 3% by the thermal motion in the crystal of potassium bromate.

5. Crystal structure of sodium bromate

The crystal structure of sodium bromate is well known. It was studied by Kolkmeijer, Bijvoet & Karssen (1920) and at least six other sets of authors since then. Abrahams & Bernstein (1977, hereafter AB77) used modern techniques with a spherical crystal to obtain anisotropic thermal parameters and good agreement with a large data set. In this context we must explain why we undertook two additional determinations of the structure of this substance.

In the initial analysis of the experiments with synchrotron radiation, described above, we failed to get good agreement between observed and calculated structure factors when we used the parameters reported by AB77. When we noticed that the thermal tensor for oxygen seemed not to be positive definite,* we collected diffraction data with one of our synchrotron specimens (crystal 4), using molybdenum radiation, and refined the atomic parameters. The resulting thermal parameters were different enough from those of AB77 that we suspected that radiation damage had occurred during the considerable time of exposure to intense radiation. Desiring to know the initial values, we repeated the structure determination using a fresh specimen (crystal 7). Our two determinations agree with each other better than either does with AB77, and there is little evidence that radiation damage has affected the results.

Crystal data: NaBrO$_3$, $M_r = 150{\cdot}9$, $P2_13$, $a = 6{\cdot}705\,(2)$ Å, $V = 301{\cdot}4\,(3)$ Å^3, $Z = 4$, $D_x = 3{\cdot}325\,(3)$, $D_m = 3{\cdot}339$ g cm^{-3} (*Handbook of Chemistry and Physics*, 1964), Mo $K\alpha$, $\lambda(\alpha_1) = 0{\cdot}70930$ Å, $\mu = 134{\cdot}2$ cm^{-1}, $F(000) = 277{\cdot}8$, $T = 296$ K, $R = 0{\cdot}013$ for 433 unique reflections (crystal 7).

---

* Lists of structure factors for both potassium bromate and sodium bromate have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39729 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* In fact the thermal tensor *is* positive definite (Abrahams, 1981), since the parameters refer to the form $\exp(-\beta_{12}hk - \ldots)$ rather than $\exp(-2\beta_{12}hk - \ldots)$ as stated by AB77.

Table 3. *Parameters for sodium bromate*

	Crystal 4	Crystal 7	AB77
$x(\mathrm{Br}^{i})$	0·40644 (3)	0·40637 (2)	0·4067 (2)
$x(\mathrm{Na}^{i})$	0·0775 (2)	0·07762 (8)	0·0775 (11)
$x(\mathrm{O})$	0·2877 (3)	0·2875 (1)	0·2882 (7)
y	0·5971 (3)	0·5969 (2)	0·5964 (7)
z	0·5084 (3)	0·5081 (1)	0·5085 (6)
$B_{11}(\mathrm{Br})$ (Å^2)	1·01 (2)	0·963 (9)	1·13 (2)
B_{12} (Å^2)	−0·055 (5)	−0·048 (3)	0·01 (3)
$B_{11}(\mathrm{Na})$ (Å^2)	1·66 (4)	1·70 (2)	2·00 (16)
B_{12} (Å^2)	−0·16 (3)	−0·18 (2)	−0·13 (20)
$B_{11}(\mathrm{O})$ (Å^2)	1·83 (6)	1·80 (3)	1·87 (11)
B_{22} (Å^2)	1·36 (6)	1·41 (3)	1·91 (11)
B_{33} (Å^2)	2·22 (7)	2·24 (4)	2·18 (11)
B_{12} (Å^2)	0·24 (6)	0·25 (3)	0·83 (9)
B_{13} (Å^2)	0·27 (5)	0·26 (3)	−0·28 (10)
B_{23} (Å^2)	−0·50 (5)	−0·50 (3)	−1·11 (8)

Symmetry code: (i) *x*, *x*, *x*.

Experimental details for crystal 7: reagent sodium bromate crystallized from water by slow evaporation. Truncated tetrahedron (5 faces) 0·13 × 0·15 × 0·18 mm; Enraf–Nonius CAD-4 diffractometer; cell dimension from 12 reflections $18 < \theta < 32°$; analytical absorption correction $2{\cdot}24 < A < 2{\cdot}84$; half sphere (*k* non-negative) to $\theta = 35°$; three standard reflections, $\sigma = 0{\cdot}018, 0{\cdot}015, 0{\cdot}019$, no correction for decay; 2548 reflections reduced to 433 unique ones $> \sigma$ including 175 Bijvoet pairs; $R_{\rm int} = 0{\cdot}040$; 9 additional unique reflections $< \sigma$ were deleted; refined on *F*; 18 parameters including f' and f'' for bromine and anisotropic thermal parameters for all atoms; $wR = 0{\cdot}012$; $S = 1{\cdot}03$; $w = 1/\sigma^2(F)$, $p = 0{\cdot}015$ in calculation of $\sigma(F^2)$; $\Delta/\sigma < 10^{-5}$; max. correction for secondary extinctions 15% of *F*. Atomic scattering factors and computer programs as for $\mathrm{KBrO_3}$.

Experimental details for crystal 4 were the same, except: 295 K, chunk with 18 faces 0·36 × 0·43 × 0·43 mm; cell dimension [a = 6·701 (2) Å] from 12 reflections $18 < \theta < 32°$; $7{\cdot}69 < A < 18{\cdot}4$; one standard reflection, $\sigma = 0{\cdot}019$; 2499 reflections reduced to 434 unique ones $> \sigma$ including 176 Bijvoet pairs; $R_{\rm int} = 0{\cdot}062$; 11 other reflections $< \sigma$ were deleted; $R = 0{\cdot}016$; $wR = 0{\cdot}026$; $S = 1{\cdot}38$; $p = 0{\cdot}03$; max. correction for secondary extinction 6% of *F*.

Atomic coordinates (Table 3) are in excellent agreement with those given by AB77. The crystal 7 results give 1·653 (1) Å, or 1·663 Å after correction for thermal motion, for the Br–O bond distance, and 104·64 (7)° for the O–Br–O angle. Thermal parameters are also in close agreement for our two determinations, but differ from those of AB77 in several cases by more than one would expect from the reported standard deviations. We cannot identify the source of these disagreements, but we point to them as a warning against overconfidence in the results of least-squares calculations with apparently good data sets. The thermal parameters do not fit molecular librations as neatly as do those of the potassium salt, but from them we estimate a r.m.s. amplitude of libration of about 4°. This much motion would reduce the anisotropy of molecular optical properties less than 1·5%, or about half as much as estimated above for potassium bromate.

Table 4. *Anomalous scattering at* Mo *Kα*

	$\mathrm{KBrO_3}$	$\mathrm{NaBrO_3}$ 4	$\mathrm{NaBrO_3}$ 7	Theory*
f' (Br)	−0·18 (11)	−0·09 (23)	−0·65 (9)	−0·374
f'' (Br)	2·51 (9)	2·53 (11)	2·55 (5)	2·456
f'' (K)	0·20 (7)	—	—	0·250

* Cromer & Liberman (1970).

Anomalous scattering terms derived from these three crystal structure refinements are compared in Table 4 with the theoretical calculations of Cromer & Liberman (1970). The scatter of the f' values indicates that their standard deviations are underestimated somewhat; this is not surprising because these parameters are strongly subject to any errors that are systematic with respect to scattering angle. The average of the three experimental f' values agrees better with theory than one could expect from the scatter. The agreement among the various f'' values is excellent.

6. Energy calibration

The photon energy and wavelength scales in this work are based on comparison with absorption spectra of sodium bromate powder, using 13 482·1 (10) eV [0·91960 (7) Å] for the first absorption peak at the bromine *K* edge. This calibration is based on Bragg angle measurements at SSRL near the bromine *K* edge and at Berkeley with Mo *Kα* radiation from a conventional source ($\lambda = 0{\cdot}70930$ Å, $K\alpha_1$), in both cases using CAD4 diffractometers and similar technique with a spherical ruby crystal (Calvert, Gabe & Le Page, 1981). The absorption edge is measured as 13 480·7 (10) eV or 0·91969 (7) Å, but we prefer the peak value as a standard because it is less subject to changes in collimation and other experimental conditions. These values are close to what we measure with the traditional method of calibration of the monochromator at the *K* edge in copper metal, but this method is affected by temperature changes in the silicon monochromator crystal in the intense synchrotron radiation. Hanawalt (1931) gives 0·9200 Å (converted from x.u.) for the *K* edge in solid sodium bromate, with 7 eV as the width of the first peak. About half of the disagreement with our value can be attributed to lower resolution in Hanawalt's experiment. The value 0·9204 Å for the *K* edge listed in *International Tables for X-ray Crystallography* (1974) comes from Hanawalt's value for bromine gas.

The photon energy was set with a precision of 0·4 eV, but it was not that stable. The f'' values in Table 1 suggest a systematic bias of *ca* 1 eV toward photon energy greater than indicated by the monochromator setting. We explain this by cooling of the monochromator as the beam intensity decays. A 10 K change of the silicon crystal is enough for a 1 eV change.

7. X-ray optical activity of sodium bromate

Optical activity in crystals at X-ray wavelengths, studied by Hart (1978) and Hart & Rodrigues (1981) in quartz and nickel sulfate hexahydrate and by Sauvage, Malgrange & Petroff (1983) in sodium bromate, is a small effect, which is difficult to measure. No reliable theoretical calculation of the magnitudes of the rotations seems to exist. Our results for the anisotropic scattering factors, which are equivalent to index of refraction values, permit some estimates of the rotation in sodium bromate as a function of wavelength.

The optical activity of sodium bromate is one of the most familiar examples of this property in cubic crystals. The specific rotation is 28° cm^{-1} at 5890 Å. This rotation is proportional to the difference of refractive index for right and left circularly polarized light and inversely proportional to wavelength in vacuum. Both circular and linear birefringence arise from the anisotropic character of atomic or molecular dielectric tensors. We expect the variation of rotation with wavelength for X-rays to be similar to the variation of f'_2. The most favorable wavelength for its observation is near 0·9205 Å. We estimate that the rotation there is about three times as much as at 0·92242 Å, where Sauvage, Malgrange & Petroff (1983) observed 0·35 (31)° cm^{-1}. At shorter wavelengths the high absorption will prevent experiments with thick crystals, and the large anisotropy of f'' is likely to induce circular dichroism, which will obscure the rotation.

We can also make a crude estimate of the magnitude of the rotation. It is only an approximation because some important details are disregarded, but it is a guide for the general order of magnitude. We use optical properties of the potassium salt. The linear birefringence (difference of principal indices of refraction) of potassium bromate in the visible is 0·079 (Swanson, Gilfrich & Cook, 1957). For 0·92 Å its real part is

$$(2\pi Ne^2/m\omega^2)f'_2 = 4{\cdot}5\times10^{-8}f'_2,$$

where N is the number of bromine atoms per unit volume. If the circular birefringence of the sodium salt changes in the same proportion, the specific rotation at 0·92 Å will be

$$(28)(5890/0{\cdot}92)(4{\cdot}5\times10^{-8}/0{\cdot}079)f'_2 = 0{\cdot}10f'_2{}^\circ\ \text{cm}^{-1}.$$

This corresponds to about 0·03° cm^{-1} at 0·92242 Å, which is less than found by Sauvage *et al.* (1983), but almost within the estimated error limit.

8. Discussion

This work demonstrates that both the magnitude of the anomalous scattering effects and their anisotropy with respect to polarization are exceptionally large for bromine in bromate ions at wavelengths near the K absorption edge. These effects arise from an absorption resonance in which a K electron is excited to a vacant electronic state. The available final states at energies near the absorption edge are molecular orbitals whose angular functions are coupled to the orientation of the ion in space, thus giving rise to the polarization dependence. The details of these excited states and of the transition probabilities to them provide inviting problems for theoretical analysis, but are beyond the scope of the present paper.

We think that to a good approximation these effects are characteristic of the bromate ion, and that they are little affected by which salt it is in. The reason is that the chemical interaction of bromine with the three oxygen atoms is very much stronger than with any neighboring ion. Even in the EXAFS region, where the more distant neighbors may contribute to the spectrum, the oxygen atoms will give the leading terms in the anisotropy of absorption. Thus we never believed that the big discrepancy between the results for the sodium and potassium salts represented a real difference in molecular properties. At first we failed to appreciate how much the imperfect polarization could affect the absorption experiment, and looked for an explanation in the thermal parameters. As discussed above, the thermal motion attenuates the anisotropy only a few percent in either salt. We also exclude harmonic radiation as a major source of error in the absorption curves presented here, although it is often an error in this kind of experiment.

These results suggest that significant X-ray dichroism may exist generally in numerous compounds that have pyramidal structures, particularly those with electronic structures similar to that of bromate. The most obvious examples are the selenite ion, SeO_3^{2-}, which is isoelectronic, and the homologous ions iodate, tellurite, *etc.* Xenon trioxide could be added to the list, but will be avoided by those familiar with its proclivity toward detonation.

We have observed even larger anisotropy of the anomalous scattering in the square-planar tetrachloroplatinate(II) ion, near the platinum L_3 edge. These experiments, to be described elsewhere, give further evidence that these effects are likely to occur in any molecule of suitable symmetry at wavelengths near an appropriate absorption edge.

The fact that effects observed here are so large makes more promising their possible application in new methods of structure determination. One can imagine the use of intensities measured at various azimuthal angles for diffraction phase determination in much the same way as the use of observations at different wavelengths or data for Bijvoet pairs. The analysis would be somewhat more complicated, but in return would give orientational information about the anisotropic molecule. The sensitivity of these effects to chemical state opens a way to differentiate atoms of the same element in different chemical states in a crystal. This may be possible even without any anisotropy if there is enough chemical shift of the absorption-edge energy, or enough difference in the strength of the resonance absorption.

These anisotropy effects may also influence, but not necessarily for the better, the use of multiple-wavelength data in studies of amorphous materials to decompose the composite radial distribution function into parts for each combination of elements (Shevchik, 1977; Fuoss, Eisenberger, Warburton & Bienenstock, 1981). In an amorphous sample, different atoms have different environments, and thus they may have different degrees of anisotropy of scattering. Large enough differences would invalidate the assumption that all atoms of one element have the same scattering power at a particular wavelength, which is part of the basis for decomposing the radial distribution function into its parts. On the other hand, someone may invent a way to use the anisotropy to gain additional information. Those using these methods should be alert to this possible complication.

A new diffraction experiment, which we wish to test, is to use a polarized source with a polarization-sensitive detector to observe the *sp* scattering component free of the other components. If this can be done, the resulting data will consist of a diffraction pattern of the dichroic atoms only. An obvious application of the *sp* diffraction pattern is to help locate heavy atoms for the isomorphous-replacement method in macromolecular problems. This use is likely to require some technical innovations before it is practical. We estimate that existing synchrotron sources are strong enough for demonstrations with simple crystals.

Our data were analyzed in the formalism of kinematic diffraction theory, which we believe is appropriate for these experiments with mosaic crystals. The molecular polarization effects considered here are quite distinct from the birefringence and dichroism, which are found when diffraction occurs in highly perfect crystals and which are explained by dynamical theory (*e.g.* Molière, 1939; Skalicky & Malgrange, 1972; Hart, 1978). The molecular effects depend on the relation of the polarization to the molecular orientation. Dynamical effects in the cases that have been studied involve only the relation of the polarization to the wave vectors of the various wave fields in the crystal, and thus their angular properties are different. They also become very small when the crystal is not in diffraction position. Dynamical theory must explain diffraction even when there is intrinsic tensor character of the dielectric constant, but it will be more complicated. For example, the wave fields may not be purely transverse, but may have some longitudinal character. It will be interesting to study the combination of these effects if suitable substances can be prepared as crystals with enough perfection.

Another simplification that we made is to neglect quadrupole terms and higher ones that may arise because the atomic dimensions are not negligible on the scale of the wavelength. Such terms are expected to change the anomalous scattering a few percent as a function of Bragg angle. A more interesting complication is that the optical properties cannot be described by a second-order tensor if multipole terms higher than dipole are significant. One result is more complicated angular functions for these properties. We verified that the spectra described here were free of any large deviation from dipole behavior. A weak quadrupole absorption, identified by its variation with beam direction, was discovered by Hahn, Scott, Hodgson, Doniach, Desjardins & Solomon (1982) in a square-planar $CuCl_4^{2-}$ complex. The effect of quadrupole absorption on diffraction phenomena is an intriguing problem for further work.

This work was supported by the National Science Foundation under grant No. CHE-8217443. It was done in part at SSRL, which is supported by the US Department of Energy, Office of Basic Energy Sciences; the National Science Foundation, Division of Materials Research; and the National Institutes of Health, Biotechnology Resource Program, Division of Research Resources; in part at the Lawrence Berkeley Laboratory, supported 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; and in part at the UC Berkeley X-ray Crystallographic Facility (CHEXRAY).

References

ABRAHAMS, S. C. (1981). Private communication.

ABRAHAMS, S. C. & BERNSTEIN, J. L. (1977). *Acta Cryst.* **B33**, 3601-3604.

CALVERT, L. D., GABE, E. J. & LE PAGE, Y. (1981). *Acta Cryst.* **A37**, C314.

COLE, H., CHAMBERS, F. W. & WOOD, C. G. (1961). *J. Appl. Phys.* **32**, 1942-1945.

COX, A. D. & BEAUMONT, J. H. (1980). *Philos. Mag.* **B42**, 115-126.

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

DMITRIENKO, V. E. (1983). *Acta Cryst.* **A39**, 29-35.

DMITRIENKO, V. E. (1984). *Acta Cryst.* **A40**, 89-95.

FUOSS, P. H., EISENBERGER, P., WARBURTON, W. K. & BIENENSTOCK, A. (1981). *Phys. Rev. Lett.* **46**, 1537-1540.

GILLESPIE, R. B., GANTZEL, P. K. & TRUEBLOOD, K. N. (1962). *Acta Cryst.* **15**, 1271-1272.

HAHN, J. E., SCOTT, R. A., HODGSON, K. O., DONIACH, S., DESJARDINS, S. R. & SOLOMON, E. I. (1982). *Chem. Phys. Lett.* **88**, 595-598.

HANAWALT, J. D. (1931). *Phys. Rev.* **37**, 715-726.

Handbook of Chemistry and Physics (1964). Cleveland: Chemical Rubber Co.

HART, M. (1978). *Philos. Mag.* **B38**, 41-56.

HART, M. & RODRIGUES, A. R. D. (1981). *Philos. Mag.* **B43**, 321-332.

HEALD, S. M. & STERN, E. A. (1977). *Phys. Rev.* **B16**, 5549-5559.

HEALD, S. M. & STERN, E. A. (1978). *Phys. Rev.* **B17**, 4069-4081.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KOLKMEIJER, N. H., BIJVOET, J. M. & KARSSEN, A. (1920). *Proc. K. Ned. Akad. Wet.* **23**, 644-653.

KUTZLER, F. W., SCOTT, R. A., BERG, J. M., HODGSON, K. O., DONIACH, S., CRAMER, S. P. & CHANG, C. H. (1981). *J. Am. Chem. Soc.* **103**, 6083-6088.

MOLIÈRE, G. (1939). *Ann. Phys. (Leipzig)*, **35**, 272-296, 297-313.

PHILLIPS, J. C., CERINO, J. A. & HODGSON, K. O. (1979). *J. Appl. Cryst.* **12**, 592-600.

SAUVAGE, M., MALGRANGE, C. & PETROFF, J. F. (1983). *J. Appl. Cryst.* **16**, 14-20.

SHEVCHIK, N. J. (1977). *Philos. Mag.* **35**, 805-809, 1289-1298.

SKALICKY, P. & MALGRANGE, C. (1972). *Acta Cryst.* **A28**, 501-507.

SWANSON, H. E., GILFRICH, N. T. & COOK, M. I. (1957). *Natl Bur. Stand. (US) Circ.* No. 539, 7, 38.

TEMPLETON, D. H. & TEMPLETON, L. K. (1980). *Acta Cryst.* **A36**, 237-241.

TEMPLETON, D. H. & TEMPLETON, L. K. (1982). *Acta Cryst.* **A38**, 62-67.

TEMPLETON, D. H. & TEMPLETON, L. K. (1984). *Am. Crystallogr. Assoc. Ann. Meet.* Abstr. V2.

ZACHARIASEN, W. H. (1928). *Skr. Nor. Vidensk. Akad. Oslo* 1, No. 4.

Acta Cryst. (1985). A**41**, 142-151

The 'Best' Unit Cell for Monoclinic Structures Consistent With *b* Axis Unique and Cell Choice 1 of *International Tables for Crystallography* (1983)

BY ERWIN PARTHÉ AND LOUISE M. GELATO

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24, quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

(*Received 28 May 1984; accepted 19 September 1984*)

Abstract

Diagrams with the c/a ratio as ordinate and $\cos(180° - \beta)$ as abscissa are given, which allow one to find out how a given monoclinic unit cell can be transformed so that **a** and **c** are the shortest translation vectors compatible with the symmetry of the space group in a setting corresponding to the standard space-group symbol given in *International Tables for Crystallography* [Vol. A. (1983). Dordrecht: Reidel] [denoted as IT(1983)], which means *b* axis unique and cell choice 1 where applicable. The diagrams contain the transformation matrices and indicate whether the origin of the transformed cell has to be shifted in order to obtain a structure description with the Wyckoff positions listed in IT (1983). A 'best' monoclinic unit cell consistent with cell choice 1 is one of the requirements for a standardized description of crystal-structure data according to Parthé & Gelato [*Acta Cryst.* (1984), **A40**, 169-183].

Introduction

This work is a complement to the earlier paper on structure data standardization (Parthé & Gelato, 1984) in so far as a simple test is given, which allows one to decide whether or not a given monoclinic cell is the correct one for the standardization of the atom coordinates.

A standardization procedure may be based on various philosophies such as relying on geometrical relationships, crystal chemical considerations or symmetry. For reasons discussed in our earlier paper we choose symmetry as the basis for our standard. The first step in the standardization of crystal-structure data is the proper choice of a unit cell. We proposed for monoclinic structures the setting that corresponds to the standard space-group symbol with *b* axis unique and cell choice 1 as given in IT (1983) and a unit-cell basis, always with β non-acute, with the following characteristics:

a relabelled Niggli reduced cell* such that *b* is the unique axis and $|\mathbf{a}| < |\mathbf{c}|$ for $P2$, $P2_1$, Pm, $P2/m$, $P2_1/m$;

a cell where **a** and **c** are the shortest translation vectors compatible with the condition of *b* axis unique and cell choice 1 for space groups Pc, $P2/c$, $P2_1/c$, $C2$, Cm, Cc, $C2/m$ and $C2/c$.

The **b**-axis setting of the space group with cell choice 1 as given in IT(1983) corresponds to the only space-group description given in *Internationale Tabellen zur Bestimniung von Kristallstrukturen* (1935) [IT(1935)] and the '2nd setting' in *International Tables*

---

* This is a Niggli reduced cell [see IT(1983), pp. 737-744] but with interchanged axes where necessary.

0108-7673/85/020142-10$01.50