In summary, we have shown that for complex polyphenyl molecules temperature factors and bond-length corrections can be calculated without extensive difficulty, using transferable force fields, as derived from a group of similar substances. Such temperature factors seem to agree very well with good experimental measurements and with other conformational data derived from solution of crystal structures. The computing time, for the whole procedure, is about 50 min on a machine like Siemens 7.865, using our set of programs (Gramaccioli & Filippini, 1985).

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X-ray Dichroism and Anomalous Scattering of Potassium Tetrachloroplatinate(II)

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Abstract

X-ray dichroism is observed at the *L* absorption edges of Pt in K_2PtCl_4, and the anomalous scattering tensor for Pt in this square-planar complex is measured in experiments with linearly polarized synchrotron radiation. For special azimuthal settings the diffraction intensities of some reflections depend on only one or the other of the principal values of the tensor. The polarization anisotropy, which is as much as 10 electrons atom^{-1} for f'', is the largest yet reported for anomalous scattering. These phenomena offer a new way to determine diffraction phases, but add complications for previous methods using multiple wavelengths.

1. Introduction

Strong X-ray dichroism can occur near an absorption edge when the absorbing atom is in a suitable molecular environment. We are interested in the polarization anisotropy of the anomalous scattering, which is another aspect of this phenomenon, and in its consequences in diffraction experiments. The tensor that describes this anomalous scattering has already been measured in diffraction experiments with the linear uranyl (UO_2^{2-}) ion (Templeton & Templeton, 1982) and the pyramidal bromate (BrO_3^-) ion (Templeton & Templeton, 1985). In both cases cubic crystals were used to avoid some of the complications that these effects introduce into the diffraction

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optics. In the present paper we report an extension of this work to the square-planar $PtCl_4^{2-}$ ion. This example was chosen for several reasons: it involves a different molecular symmetry; it has been used to make heavy-atom derivatives in macromolecular crystallography; its potassium salt has a simple tetragonal structure that is convenient for polarized absorption spectroscopy and that allows a test of diffraction optics in non-cubic symmetry without the full complications of the general case; and we speculated that it would exhibit significant dichroism. In fact its dichroism is the strongest that we have yet observed.

These experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL). Synchrotron radiation has several properties essential for this work: strong linear polarization, continuous spectrum that permits free choice of wavelength, and enough intensity for high wavelength resolution.

2. Diffraction with uniaxial symmetry

In a crystal of K_2PtCl_4 all the $PtCl_4^{2-}$ ions have identical orientations with c as the direction of the unique symmetry axis. If we consider only dipole scattering in the kinematic approximation, the X-ray optical properties are like those described as 'uniaxial' in traditional crystal optics except that the small wavelength permits diffraction to occur. It follows that the details of beam propagation and scattering are simpler for certain special settings than for the general case, just as is true in the visible wavelengths.

We consider an incident horizontal beam with some degree of horizontal linear polarization, and scattering in the vertical plane. As a coordinate system take x perpendicular to the plane of scattering, z parallel to $\mathbf{h}=(hkl)$, and y perpendicular to x and z. Define three polarization unit vectors as:

$$\mathbf{s}=\begin{pmatrix}1\\0\\0\end{pmatrix},\ \mathbf{p}=\begin{pmatrix}0\\-\sin\theta\\\cos\theta\end{pmatrix},\ \mathbf{p}'=\begin{pmatrix}0\\\sin\theta\\\cos\theta\end{pmatrix}. \qquad (1)$$

We use $\mathbf{s}$ and $\mathbf{p}$ to describe the polarization of the incident beam and $\mathbf{s}$ and $\mathbf{p}'$ for the scattered beam. As in Templeton & Templeton (1982) the various scattering factors for the dichroic atom are given by

$$f_{ee'}=\mathbf{e}^T\mathbf{f}\mathbf{e}', \qquad (2)$$

where $\mathbf{e}$ is $\mathbf{s}$ or $\mathbf{p}$, $\mathbf{e}'$ is $\mathbf{s}$ or $\mathbf{p}'$, and $\mathbf{f}$ is the scattering-factor tensor. The site symmetry of the platinum atom in this example is $4/mmm$. Thus the tensor $\mathbf{f}$ takes the simple form

$$\mathbf{f}=\begin{pmatrix}f_\pi & 0 & 0\\0 & f_\pi & 0\\0 & 0 & f_\sigma\end{pmatrix} \qquad (3)$$

when the fourfold axis of the crystal coincides with the z axis of the coordinate system. The elements of this matrix are complex numbers:

$$f_\pi=f_0+f'_\pi+if''_\pi \quad \text{and} \quad f_\sigma=f_0+f'_\sigma+if''_\sigma. \qquad (4)$$

The atomic absorption parameter for polarization $\mathbf{e}$ is proportional to the imaginary part of the amplitude for forward scattering (James, 1982), calculated with $\mathbf{e}'=\mathbf{e}$:

$$\mu_a(\mathbf{e})=(4\pi e^2/m\omega c)\ \mathrm{Im}\ (\mathbf{e}^T\mathbf{f}\mathbf{e}). \qquad (5)$$

In our previous work with cubic crystals these choices of polarization vectors were appropriate for any orientation of the crystal. For a crystal with significant birefringence for X-rays, as in the case of visible light, simple treatment of the propagation requires polarization vectors that are principal directions of the transverse section of the optical tensor. The vectors in (1) have this property only for certain special orientations of the crystal, some of which we now describe. For diffraction by any Bragg plane hkl in K_2PtCl_4 there exist two values (180° apart) of the azimuthal angle ψ that place the c axis in the plane of scattering. We designate such orientations as 'π' settings, and show in the Appendix a method for calculating them. For $00l$ planes, any value of ψ gives a π setting, and $\mathbf{f}$ is given by (3). For any π setting, since the x axis is perpendicular to c, $\mathbf{f}$ takes the form

$$\mathbf{f}(`\pi')=\begin{pmatrix}f_\pi & 0 & 0\\0 & f_{22} & f_{23}\\0 & f_{23} & f_{33}\end{pmatrix}. \qquad (6)$$

If only $hk0$ reflections are considered, $\mathbf{h}$ is perpendicular to c and $\mathbf{f}(`\pi')$ is diagonal:

$$\mathbf{f}(`\pi', hk0)=\begin{pmatrix}f_\pi & 0 & 0\\0 & f_\sigma & 0\\0 & 0 & f_\pi\end{pmatrix}. \qquad (7)$$

An azimuthal rotation of 90° from the π setting gives the 'σ' setting for a reflection $hk0$; since this rotation interchanges f_{11} and f_{22},

$$\mathbf{f}(`\sigma', hk0)=\begin{pmatrix}f_\sigma & 0 & 0\\0 & f_\pi & 0\\0 & 0 & f_\pi\end{pmatrix}. \qquad (8)$$

We are particularly interested in incident X-rays with 100% s polarization. Then only f_{ss} and $f_{sp'}$ need be considered. This $f_{sp'}$ is identical with f_{sp} used in earlier papers, where our notation was less explicit (Templeton & Templeton, 1982). Substitution of (1) and (6) or (8) into (2) gives

$$f_{ss}(`\pi')=f_\pi, \qquad f_{ss}(`\sigma', hk0)=f_\sigma$$

and

$$f_{sp'}(`\pi')=f_{sp'}(`\sigma', hk0)=0. \qquad (9)$$

Thus in each case the scattered ray is also purely s polarized. For both incident and scattered rays, (5) shows that μ_a corresponds to the respective π or σ value of f''. A set of diffraction data recorded under these conditions (limited to $hk0$ for 'σ') can be analyzed to derive the respective principal values of f' and f'' for platinum by the method we have used in the absence of dichroism (Templeton, Templeton, Phizackerley & Hodgson, 1982).

We must also consider imperfectly polarized radiation. For the 'σ' setting,

$$f_{pp'}(\text{`}\sigma\text{'}, hk0) = f_\pi \cos 2\theta, \qquad f_{ps} = 0, \tag{10}$$

and μ_a for both p and p' rays corresponds to f''_π. For 'π' settings f_{ps} is again zero, but $f_{pp'}$ is more complicated, even when restricted to $hk0$ reflections:

$$f_{pp'}(\text{`}\pi\text{'}, hk0) = f_\pi \cos^2\theta - f_\sigma \sin^2\theta \tag{11}$$

$$= \tfrac{1}{2}(f_\pi + f_\sigma)\cos 2\theta + \tfrac{1}{2}(f_\pi - f_\sigma). \tag{11a}$$

Again the absorption parameter is the same for p and p' polarizations, but now it is a function of θ:

$$\mu_a(pp, \text{`}\pi\text{'}, hk0) = \mu_\pi \cos^2\theta + \mu_\sigma \sin^2\theta. \tag{12}$$

3. Crystal structure of potassium tetrachloroplatinate(II)

The crystal structure of K_2PtCl_4 was determined by Dickinson (1922) and has been further refined with anisotropic thermal parameters by Mais, Owston & Wood (1972) and Ohba, Sato, Saito, Ohshima & Harada (1983). We refined it again to get parameters that were based on exactly the same atomic form factors as those used to fit the synchrotron diffraction data. Our results are in excellent agreement with the last two studies cited above. Note, however, that Ohba *et al.* misquote the value obtained by Mais *et al.* for U_{12} of Cl.

Crystal data. K_2PtCl_4, $M_r = 415{\cdot}1$, tetragonal, $P4/mmm$, $a = 7{\cdot}023\,(1)$, $c = 4{\cdot}1486\,(4)$ Å, $V = 204{\cdot}62$ Å^3, $Z = 1$, $D_m = 3{\cdot}382$ g cm^{-3} (Klement, 1927), $D_x = 3{\cdot}368\,(1)$ g cm^{-3}, Mo $K\alpha$, $\lambda(\alpha_1) = 0{\cdot}70930$ Å, $\mu = 195{\cdot}6$ cm^{-1}, $F(000) = 184$, $T = 297$ K, $R = 0{\cdot}026$ for 675 reflections. Pt: 0, 0, 0; $U_{11} = 182\,(1)$, $U_{33} = 214\,(1)$; K: $0, \frac{1}{2}, \frac{1}{2}$; $U_{11} = 460\,(6)$, $U_{22} = 308\,(4)$, $U_{33} = 262\,(3)$; Cl: $x, x, 0$; $x = 0{\cdot}23247\,(8)$; $U_{11} = 237\,(1)$, $U_{33} = 408\,(3)$, $U_{12} = -31\,(2)$; all U's $\times 10^4$ Å^2.

Experimental. Crystallization from water yielded a triangular plate, $0{\cdot}50 \times 0{\cdot}40 \times 0{\cdot}066$ mm with (100) and ($\bar{1}00$) as the largest faces. Cell dimensions from 14 reflections in θ range 31 to 38° centered with Picker FACS-I. Intensity data from Enraf-Nonius CAD-4; correction factors for absorption by the analytical method (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973) in range 3·1 to 26·7; max. $(\sin\theta)/\lambda = 1{\cdot}077$ Å^{-1}; hkl ranges -15 to 15, -15 to 0, 0 to 8; standard reflections (600, 0$\bar{6}$0, 004), $\sigma = 0{\cdot}01$; no correction for decay; 2386 observations averaged to give 680 unique reflections, none weaker than 2σ, 5 strong ones omitted; $R(F)_{\text{int}} = 0{\cdot}035$, known structure refined on F, ten parameters; $wR = 0{\cdot}028$, $S = 1{\cdot}19$, $w = [\sigma(F)]^{-2}$, derived from $\sigma^2(F^2) = \{[\sigma(F^2)$, counting statistics only$] + (0{\cdot}03\,F^2)^2\}$; max. $(\Delta/\sigma) < 10^{-5}$; max. empirical isotropic correction for extinction 15% of F; atomic f (including f' and f'') for Pt, K^+ and $Cl^{0{\cdot}5-}$ (interpolated) from *International Tables for X-ray Crystallography* (1974), local unpublished programs.*

4. Polarized diffraction and absorption experiments

Polarized absorption spectra at the platinum L edges (Figs. 1–3) were measured by a method described by Templeton & Templeton (1980). The K_2PtCl_4 specimen was a flat crystal, *ca* $0{\cdot}15 \times 0{\cdot}75 \times 1{\cdot}25$ mm, with (100) as its largest face.

Diffraction experiments with synchrotron radiation were made at wavelengths near the Pt L_3 absorption edge using the same crystal as in the structure determination described above. The photon energy and wavelength scales in this work are based on absorption spectra of K_2PtCl_4 powder, assuming 11·562 keV (1·0723 Å) for the Pt L_3 absorption edge (Bearden, 1967). Beam line II-2 at SSRL was used without any focusing mirror (to avoid degradation of the wavelength resolution) and with a double-crystal Si(111) or Si(220) monochromator (Hastings, Kincaid & Eisenberger, 1978). Contamination by harmonic wavelengths was reduced by slight misalignment of the two monochromator crystals (Bonse,

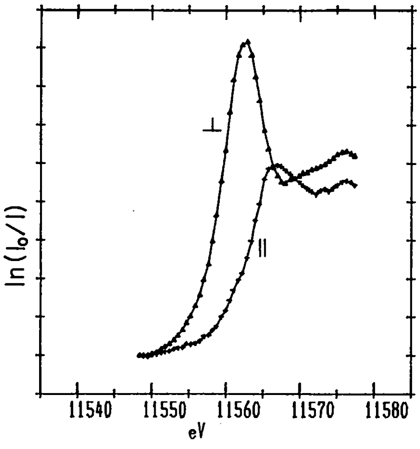

Fig. 1. Absorption coefficient (on an arbitrary scale) *versus* photon energy for polarized X-rays with electric vector parallel and perpendicular to the fourfold axis of $PtCl_4^{2-}$ near the platinum L_3 absorption edge.

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* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42011 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Materlik & Schröder, 1976), by discrimination of the pulses from the scintillation detector, and in the case of Si(111) by the weak intensity of the second order. The angle of this monochromator was set with a stepping motor with 2000 steps/°. The position of the peak of the strong absorption line near the L_3 edge could be reproduced with a precision of one motor step over short time intervals, but sometimes not over periods of hours. A defect of this monochromator, corrected in some later models, is that the stepping motor controls the first crystal (which is subject to heating by the white radiation) rather than the second one (whose temperature is more nearly constant). The angle between the two crystals is set by an adjustment without any numerical scale. In a typical 'parallel' experiment, the Enraf-Nonius CAD-4 diffractometer (Phillips, Cerino & Hodgson, 1979) was used in the 'file' mode with a value of ψ for each of 71 reflections calculated according to the 'σ' setting. Some experiments used a shorter list. Each tenth reflection was 10,0,0 as an intensity standard. The remaining 63 reflections, all of type $hk0$, included 56 independent ones in the range $2\theta = 27$ to 121°, plus a few symmetry-equivalent ones. The experiment was repeated immediately one or more times. The incident beam passed through an ion chamber. Readings, at intervals of 10 s, were used to scale the intensities for beam changes. Sometimes the ion-chamber readings did not change in the same way as the standard reflections because they sampled a larger cross section of beam. If so, the standard reflections were used for further scaling. A measurement was rejected if it failed the 'not equal' test (a comparison of forward and backward scans that detects beam fluctuations of short duration), if it were marked 'too weak' or 'too strong' by the data-collection program, if it coincided with severe instability of the beam, or if it failed to check a duplicate measurement. In some cases one or two reflections that suffered from extinction were deleted.

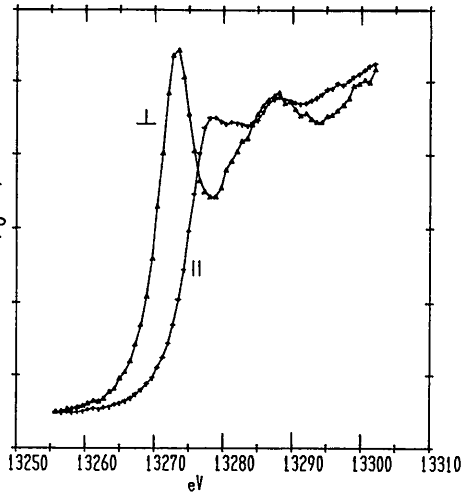

Fig. 2. Same as Fig. 1, but near L_2 edge.

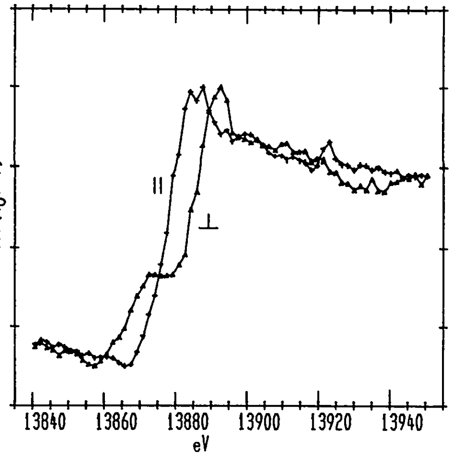

Fig. 3. Same as Fig. 1, but near L_1 edge.

The same methods were used for perpendicular experiments, but π settings were used, and a few reflections of type $hk1$ were included.

Several sets of measurements were made using 'zigzag' mode with $\psi = 0$ at wavelengths where little polarization anisotropy was expected. They were analyzed assuming an isotropic model of the optical properties. The results are expected to approximate the weighted average value, $(f_\sigma + 2f_\pi)/3$.

Intensities were corrected for absorption by analytical integration. Since f'', and hence the absorption parameter, is being measured in these experiments, the process is somewhat circular. Tests showed, however, that the results for f'' are not sensitive to the value of μ used in the absorption correction. The agreement index R is more sensitive to it. No correction was made for polarization.

Each data set was refined by the method of least squares with f' and f'' for platinum, an empirical isotropic extinction parameter, and a scale factor as variables. In some cases f'' was held at an assumed value because it was not well determined by the data set. For this centrosymmetric structure, intensities are not sensitive to f'' if its value is small or if no weak reflections are included. Results are listed in Tables 1, 2 and 3 and plotted in Fig. 4.

The scattering factors are extremely sensitive to wavelength near the absorption edge. In the experiments in June 1983, we had difficulty in holding the wavelength with enough precision at the values set by the absorption-curve calibration. The results are in better agreement if some wavelengths, marked in the tables as 'in doubt', are changed by 0·0001 or 0·0002 Å. These amounts correspond to less than two or three steps of the stepping motor that sets the monochromator.

Table 1. *Anomalous scattering of platinum, parallel polarization*

λ(Å)	f'_σ	f''_σ	*R* (%)	*N**	Date†
1·07152	−14·0 (10)	[10·45]‡	6·2	46	*A*
1·07182	−16.9 (10)	9·7 (7)	4.2	56	*B*
1·07184	−16.2 (8)	[10·87]	5·1	46	*A*
1·07198	−17·8 (9)	9·0 (7)	5·7	57	*B*
1·07200	−15·2 (7)	[8·93]	6·3	46	*A*
1·07211	−19·5 (4)	7·6 (3)	5·9	55	*B*
1·07216	−17·0 (6)	[7·08]	6·2	46	*A*
1·07219?§	−18·7 (4)	6·0 (3)	4·6	55	*C*
1·07227	−19·3 (3)	6·3 (2)	4·7	57	*B*
1·07230?§	−19·2 (3)	5·9 (2)	5·2	56	*C*
1·07232	−18·9 (4)	[6·07]	5·5	46	*A*
1·07233	−19·7 (6)	5·5 (7)	5·1	54	*B*
1·07240	−18·7 (4)	5·6 (2)	5·9	57	*B*
1·07241?§	−18·9 (3)	6·0 (2)	5·4	57	*C*
1·07248	−17·5 (5)	[5·05]	6·5	46	*A*
1·07249	−18·4 (3)	4·9 (2)	5·4	57	*B*
1·07262	−18·1 (5)	[3·9]	6·5	57	*B*
1·07378	−16·6 (5)	[3·9]	5·4	55	*B*

* Number of independent reflections.

† *A* = March 1982, Si(111) monochromator; *B* = March 1983, Si(220); *C* = June 1983, Si(111).

‡ Values in brackets were assumed.

§ Wavelength in doubt; not included in Fig. 4.

Table 2. *Anomalous scattering of platinum, perpendicular polarization*

λ(Å)	f'_π	f''_π	*R* (%)	*N**	Date†
1·07152	−16·4 (5)	9·7 (3)	3·1	55	*A*
1·07184	−14·4 (7)	9·8 (4)	3·4	55	*A*
1·07200	−13·4 (9)	10·8 (6)	3·8	55	*A*
1·07203?§	−15·3 (7)	16·0 (2)	2·4	68	*C*
1·07211	−12·3 (10)	13·4 (5)	3·0	68	*B*
1·07216	−15·2 (8)	13·1 (4)	3·1	55	*A*
1·07219?§	−17·2 (5)	15·8 (2)	2·2	68	*C*
1·07227	−16·7 (8)	16·0 (3)	3·2	68	*B*
1·07230?§	−20·1 (3)	14·9 (2)	2·0	68	*C*
1·07232	−18·8 (6)	16·8 (3)	2·6	55	*A*
1·07240	−21·2 (5)	14·1 (3)	3·3	68	*B*
1·07241?§	−19·6 (4)	15·4 (2)	2·4	68	*C*
1·07248	−22·2 (4)	13·7 (2)	2·7	55	*A*
1·07249	−23·1 (5)	10·6 (3)	5·6	68	*B*

*†§ See Table 1 footnotes.

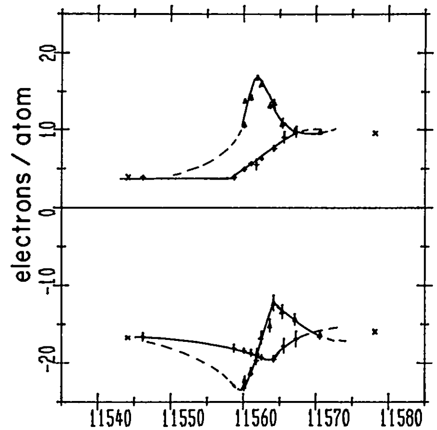

Fig. 4. Values of f'' (above) and f' (below) for Pt near the L_3 edge, derived from diffraction experiments. Points are represented by ▲ for f_π, + for f_σ, × for average values from 'zigzag' experiments. Note the resemblance of the f'' curves to the spectra in Fig. 1.

Table 3. *Anomalous scattering of platinum, isotropic model*

λ(Å)	f'		f''		*R* (%)	*N**	Date†
	exper.	theor.¶	exper.	theor.¶			
1·06826	−12·9 (5)	−14·2	10·8 (3)	10·1	5·4	129	*C*
1·07027	−17·0 (4)	−15·7	9·1 (2)	10·2	5·9	108	*B*
1·07082	−16·0 (2)	−16·4	9·5 (1)	10·2	5·2	129	*B*
1·07397	−16·7 (2)	−15·7	[3·9]	3·9	5·3	68	*C*
1·07721	−13·36 (9)	−13·7	[3·9]	3·9	4·1	190	*C*
1·08009	−12·8 (1)	−12·8	[3·9]	3·9	3·8	128	*B*

*†‡ See Table 1 footnotes.

¶ Cromer (1983).

5. Effect of incomplete polarization

Measurements of the beam polarization (Templeton & Templeton, 1984) using the Borrmann effect show that it is about 95% at the center of the beam and about 90% at 1 mm above or below, in agreement with theory for plausible values of accelerator parameters. The experiments reported here were done before we were aware that the polarization is so sensitive to alignment, and the centering procedure may not have achieved the maximum polarization. We believe that the crystal was always within 1 mm of the beam center so that the polarization was no less than 90%. That is, between 2.5 and 5% of the incident photons had *p* rather than *s* polarization. Thus a little π character is included in the values obtained for f_σ, and a little σ character in those for f_π.

The effect of this imperfect polarization is reduced considerably in the diffraction experiments by a factor $\cos^2 2\theta$, which reduces the intensity of the p' ray. This factor is exact for 'σ' settings and a good approximation for 'π' settings. Its average value for the reflections in the various data sets ranges from 0·20 to 0·29. For most of the 'σ' experiments the effect is further reduced by the greater absorption for π polarization. For 'π' experiments absorption makes matters worse, but this is more than compensated for by the considerable π character of f_{pp}, according to (11). Considering all these factors, we estimate that the anisotropy is underestimated by 1 or 2% in the diffraction experiments, an amount less than the estimated inaccuracy.

The effect on the absorption spectra is more serious because a small amount of more penetrating radiation becomes important with a thick specimen. Thus the height of the peak in the perpendicular spectrum is underestimated (Fig. 1), as is the anisotropy derived from it. Values from the two methods are compared in Fig. 5 for $(f''_\sigma - f''_\pi)$ and in Fig. 6 for $(f'_\sigma - f'_\pi)$.

6. Discussion

The polarized absorption spectra at all three *L* absorption edges exhibit strong dichroism. The L_3 and L_2 spectra are quite similar, in accord with the fact that each involves excitation of a 2*p* electron; the L_1 spectrum, involving excitation of a 2*s* electron, is quite different. The largest absolute change of cross section is at the L_3 edge, which has the largest edge jump. That is why we chose it for the diffraction experiments. It is evident that these spectra give symmetry information about the excited electronic states of $PtCl_4^{2-}$, but that subject is beyond the scope of this paper.

Dichroism will also occur in the EXAFS regions at photon energies above each edge, and it may be a useful tool in some applications of the EXAFS method. It will not, however, affect X-ray optical properties nearly as much as the edge resonances.

This work adds further evidence that X-ray dichroism is a common phenomenon near absorption edges of atoms that are on sites of less-than-cubic point symmetry, and that the effects on X-ray optical properties may be quite substantial. It also demonstrates for the first time for a non-cubic case that observed diffraction intensities are in reasonable agreement with calculations based on the second-order-tensor model in the kinematic approximation.

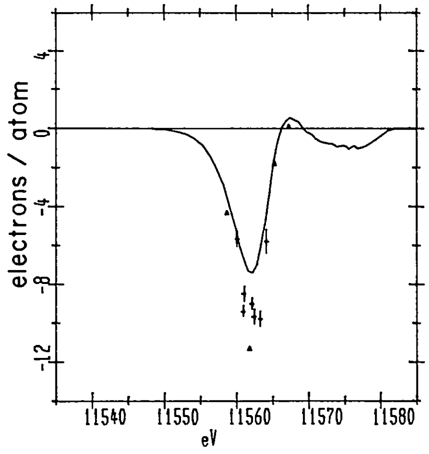

Fig. 5. Polarization anisotropy, $f''_\sigma - f''_\pi$, *versus* photon energy. Points indicate values from the diffraction experiments; those without error bars involve interpolation. The continuous curve is derived from the spectra in Fig. 1; its smaller amplitude is explained by the imperfect polarization of the radiation, as explained in the text.

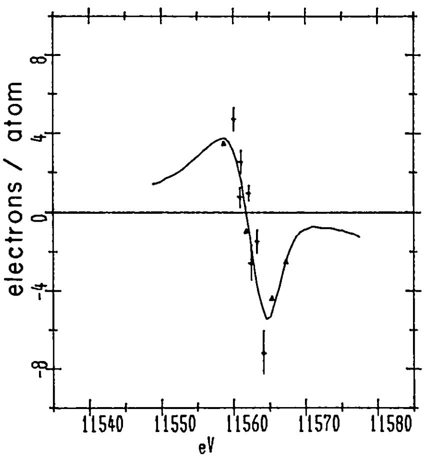

Fig. 6. Plot of $f'_\sigma - f'_\pi$ *versus* photon energy; points from diffraction experiments, curve calculated from curve in Fig. 5 by integration of the dispersion relation.

The R values listed in the tables range from 0·020 to 0·065. Much of the excess over 0·02 (perhaps all of it) must be blamed on the instabilities of the synchrotron beam in wavelength, brightness and polarization and on defects of the very large corrections for absorption. A few experiments that gave R values above 0·10 and that were clearly subject to instabilities are omitted from the tables. We note that the R values for parallel polarization (Table 1) are larger than for perpendicular (Table 2), but this may simply reflect a less satisfactory absorption correction for these setting angles, or some other systematic defect of the apparatus. Better experiments will be required to establish if any of the residual disagreement reflects the need for a better optical model.

Several consequences and possible applications of this kind of polarization anisotropy in structure research have already been discussed by Templeton & Templeton (1985). The large effects observed here add emphasis to that discussion. One of these applications is to use diffraction intensities measured at different azimuthal settings to gain information concerning diffraction phases in much the same way as from measurements at diverse wavelengths, chosen to exploit changes in the real and imaginary parts of f. The algebraic methods for this polarization method are similar to those for the multiple-wavelength method, particularly when the crystal contains only one orientation of the anisotropic scatterer as in this example. The differences are rather obvious, and need not be set forth here.

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APPENDIX

Azimuthal angles for π and σ settings

The objective is to find the azimuthal angle ψ for a reflection **h** such that a special direction **d** (specified in reciprocal-space components; 0, 0, 1 in the case of K_2PtCl_4) lies in the plane of scattering or perpendicular to it. The angles and coordinate system used here are defined as for the Enraf-Nonius CAD-4 diffractometer; this coordinate system is not the same as that used in the main text. First calculate Eulerian setting angles ϕ and χ for $\psi = 0$. For these angles **h** is along the y axis and the direction of **d** is $\mathbf{s} = \mathbf{XZRd}$, where **R** is the reciprocal-space orientation matrix and

$$\mathbf{s} = \begin{pmatrix} s_1 \\ s_2 \\ s_3 \end{pmatrix}, \mathbf{X}(\chi) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\chi & \sin\chi \\ 0 & -\sin\chi & \cos\chi \end{pmatrix},$$

$$\mathbf{Z}(\phi) = \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

An azimuthal rotation about the y axis by an angle ψ,

$$\psi = \tan^{-1}(s_3/s_1),$$

places **d** in the xy plane (the plane of scattering); this is called a π setting. If **d** is perpendicular to **h** ($hk0$ reflections in K_2PtCl_4) it is moved into coincidence with the z axis by a further rotation of ±90° of ψ; this is called a σ setting.

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Symmetry of Bicrystals Corresponding to a Given Misorientation Relationship

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Abstract

A methodology is described that enables the determination of symmetry groups of bicrystals manufactured from a given dichromatic complex. The dichromatic symmetry group is sectioned by a unique two-sided plane corresponding to the planar grain boundary and the symmetry elements of the bicrystal are established as those symmetry elements of the dichromatic group that leave the sectional plane invariant. The procedure is employed for investigating generic relations for bicrystals whose components have a given misorientation relationship. It is demonstrated that, for a dichromatic complex with point symmetry higher than 1, bicrystals of identical symmetry can be created by more than one crystallographically equivalent interfacial plane. Finally, a new scheme is proposed for the classification of grain boundaries. This scheme provides a comprehensive framework for describing the variation of bicrystal symmetry due to changes in the orientation and/or position of the associated interfacial plane.

1. Introduction

Grain boundaries are two-dimensional features separating two misorientated and displaced crystals of identical structure. In the crystallographic framework of grain-boundary symmetry (Pond &

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