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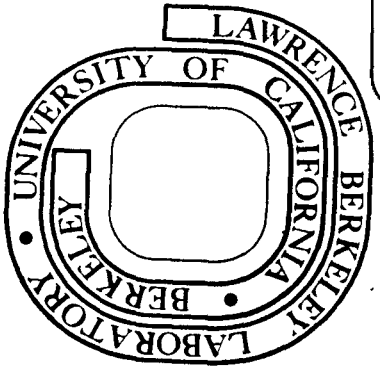

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L_{III} - Edge Anomalous Scattering of Cesium Measured with Synchrotron Radiation

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Abstract. Diffraction of monochromatized synchrotron radiation by crystals of cesium hydrogen tartrate has been used to measure the magnitude and phase of X-ray scattering for cesium near the L_{III} absorption edge. In this wavelength region the scattering amplitude of cesium is reduced by as much as 25 electrons/atom, compared to scattering of Cu Kα X-rays. This change, which varies as a function of wavelength, affects the diffraction intensities in a manner like isomorphous substitution, and it is large enough to have promise for phase determination in the study of macromolecular structures. This experiment also demonstrates that accurate diffractometer measurements are possible with synchrotron radiation produced by an electron storage ring.

We report the first X-ray diffraction experiments carried out with an automatic diffractometer and a focused monochromatic X-ray beam of synchrotron radiation from the SPEAR storage ring at the Stanford Synchrotron Radiation Laboratory (1). Diffraction measurements with crystals of cesium hydrogen (+)-tartrate have shown that this equipment can give reproducible results at wavelengths chosen from the continuous spectrum of the synchrotron radiation. We have derived from these data the anomalous scattering terms for cesium near the L_{III} absorption edge and find that the scattering power of cesium is reduced by as much as 25 electrons. This is the largest such effect yet observed in an X-ray diffraction experiment. This reduction in scattering power, which is approximately equivalent to removing a rubidium atom from the structure, could be used as a substitute for or a complement to isomorphous replacement in solving the phase problem for macromolecular structures. This technique has the advantage that the crystal structure is exactly the same as that studied at another wavelength, thus avoiding the imperfect isomorphism which generally occurs when atoms are added to or replaced in the crystal.

An atom scatters X-rays with an amplitude and phase which can be represented by the complex number $f = f_o + f' + if''$, where f_o is the value appropriate for very short wavelengths (2). The anomalous scattering terms f' and f'', which are functions of the wavelength, describe the in-phase and out-of-phase components of the change due to finite binding energies of the electrons in the atom. While f_o decreases as the scattering angle increases, f' and f'' are nearly independent of angle.

The f" term results in the breaking of Friedel's law. With an appreciable f" contribution the hkl and $\bar{h}\bar{k}\bar{l}$ reflections for non-centrosymmetric structures are no longer equal. This effect has long been used to determine absolute polarity (3), absolute configuration (4) and to provide protein phase information (5). There has been little use of f' as one needs to collect data at different wavelengths in order for it to have a useful effect on the diffraction pattern.

Near an absorption edge of an atom, where the X-ray energy is close to an inner shell electron binding energy, both f' and f" vary rapidly with wavelength; f" jumps rapidly up to a maximum while f' dips and then rises again as the X-ray energy goes from below to above the edge. Absorption edges are thus useful for phasing as f" can be maximized for maximum Friedel pair differences and a large change in f' can be obtained with a small change in incident beam energy. The recent availability of synchrotron radiation as a tunable source of X-rays made it possible to use these effects to obtain phase information from diffraction patterns from macromolecules (6) and prompted this present study.

We measure f' and f" by adjusting calculated structure factors to fit observed values, using the method of least squares with these two quantities and a scale factor as the only independent variables. Cesium hydrogen (+)-tartrate, which crystallizes in space group $P2_12_12_1$, was chosen for its desirable physical properties and favorable symmetry. Its lattice parameters, atomic coordinates, and thermal parameters are known very accurately from an experiment with MoKα radiation and conventional methods (7). The values of f' and f" for

the light atoms can be estimated with sufficient accuracy from calculations at other wavelengths (8); they are small and insensitive to wavelength in the region of interest here.

The synchrotron radiation used in this study is focused by a doubly-curved mirror and monochromatized by a rapidly-tunable two-crystal germanium (111) monochromator (9). An Enraf-Nonius CAD4 diffractometer is mounted behind the monochromator on a motorized carriage which is used to align the diffractometer to the X-ray beam (see Fig. 1). A PDP 11/34 computer controls the diffractometer, the monochromator and the alignment carriage. To align the diffractometer we developed a program to move the carriage until the beam passing through the collimator into the detector (at $2\theta = 0$) is maximized in intensity. The diffractometer is mounted with the 2θ arm swinging in the vertical plane, because the polarization vector of the synchrotron radiation is almost completely horizontal.

The x-ray beam intensity is proportional to the electron beam current and drops as the stored beam slowly decays. We monitored this intensity variation using an ion chamber placed in the beam and normalized the diffracted intensities accordingly. To calibrate the wavelength of the monochromator we measured the absorption of a sample of cesium chloride as a function of the monochromator setting. A large jump in the ratio of incident to transmitted intensity identifies the exact position of the absorption edge of cesium.

We collected diffraction data from two crystals of cesium hydrogen tartrate, a needle with 15 sharply defined faces and

dimensions about 0.093 × 0.110 × 0.40 mm and a nearly spherical crystal with mean diameter 0.28 mm. With the needle we measured 16 or 17 independent reflections in the θ-angle range 18-40° for each of three wavelengths. With the sphere, 15 to 17 independent reflections in the θ-angle range 40-48° were measured in each experiment. In each case, most of the measurements were duplicated by repetition and with equivalent reflections. With absorption parameters in the range 300 to 720 cm^{-1}, correction for absorption is critical, with factors ranging up to 49 for the needle. With the sphere the absorption effect is more nearly the same for all reflections, and the values of the corrections are less important.

The results of the least squares calculations are listed in Table I. The agreement between data from the two crystals gives us confidence that absorption is not a serious source of bias in the results.

The values of f" at the longest wavelength are similar to 3.565 calculated by Cromer and Liberman for La at CrKα, a reasonably similar case (8). The other f" values are also plausible. We know of no previous measurements or calculations of f' as negative as those listed here. At the K edge of Cu, where fewer electrons are involved, values lower than -8 have been reported (10). For gallium at the K edge -10 has been observed (11). In the latter case the maximum negative value of f' occurs close to the inflection point of the rising wave of f". Our extreme value of f' occurred at the inflection point of the rising absorption curve of cesium.

Our results are compared in Fig. 2 with values for some wavelengths available from conventional X-ray sources, to show how much the scattered wave amplitude is reduced at this L absorption edge.

The resolution of the monochromator (9) is approximately $\Delta\lambda/\lambda = 10^{-3}$. Thus we are measuring f' averaged over this wavelength range. It is possible that with a more monochromatic beam an even larger negative value of f' could be observed. This method is general, and similar experiments can be carried out with other elements at either the K or L edges.

References and Notes

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Table I. Anomalous scattering terms for cesium.

λ, Å	Crystal	R[a]	f'	f"
2.470	needle	0.086	-16.1 ± 2.6	11.1 ± 2.2
2.473[b]	needle	0.067	-24.5 ± 1.2	5.9 ± 0.7
	sphere	0.083	-27.1 ± 0.9	4.9 ± 0.6
2.477	needle	0.060	-19.9 ± 0.9	3.5 ± 0.5
	sphere[c]	0.049	-21.4 ± 0.6	3.8 ± 0.3
	sphere[d]	0.034	-20.8 ± 0.5	4.1 ± 0.3

[a] $R = \Sigma|\Delta F|/\Sigma|F_o|$.

[b] Inflection point of L_{III} edge, measured with CsCl.

[c,d] Two different experiments, with different storage ring conditions and different mechanical adjustment of the monochromator.

Figure Captions

Fig. 1. View of the experimental apparatus. The tank housing the two crystal monochromator is seen on the right. The monochromatized x-ray beam enters the hutch (which has one side removed to permit view of the inside) and into the entrance collimator of the diffractometer. The diffractometer is supported by the computer controlled carriage seen in the lower part of the hutch. The two theta arm holding the detector can be seen below the median plane and the film carousel (which is removed when the detector is being used) is to the left.

Fig. 2 Atomic scattering vectors for cesium for $(\sin\theta)/\lambda = 0.3\ \text{Å}^{-1}$, where $f_o = 38$. The length of each vector represents the amplitude of the wave scattered by the atom, and the angle from the horizontal represents the phase shift relative to scattering by a free electron. The circles represent our experimental points. The other vectors are calculated (8) for some wavelengths available from conventional X-ray tubes.

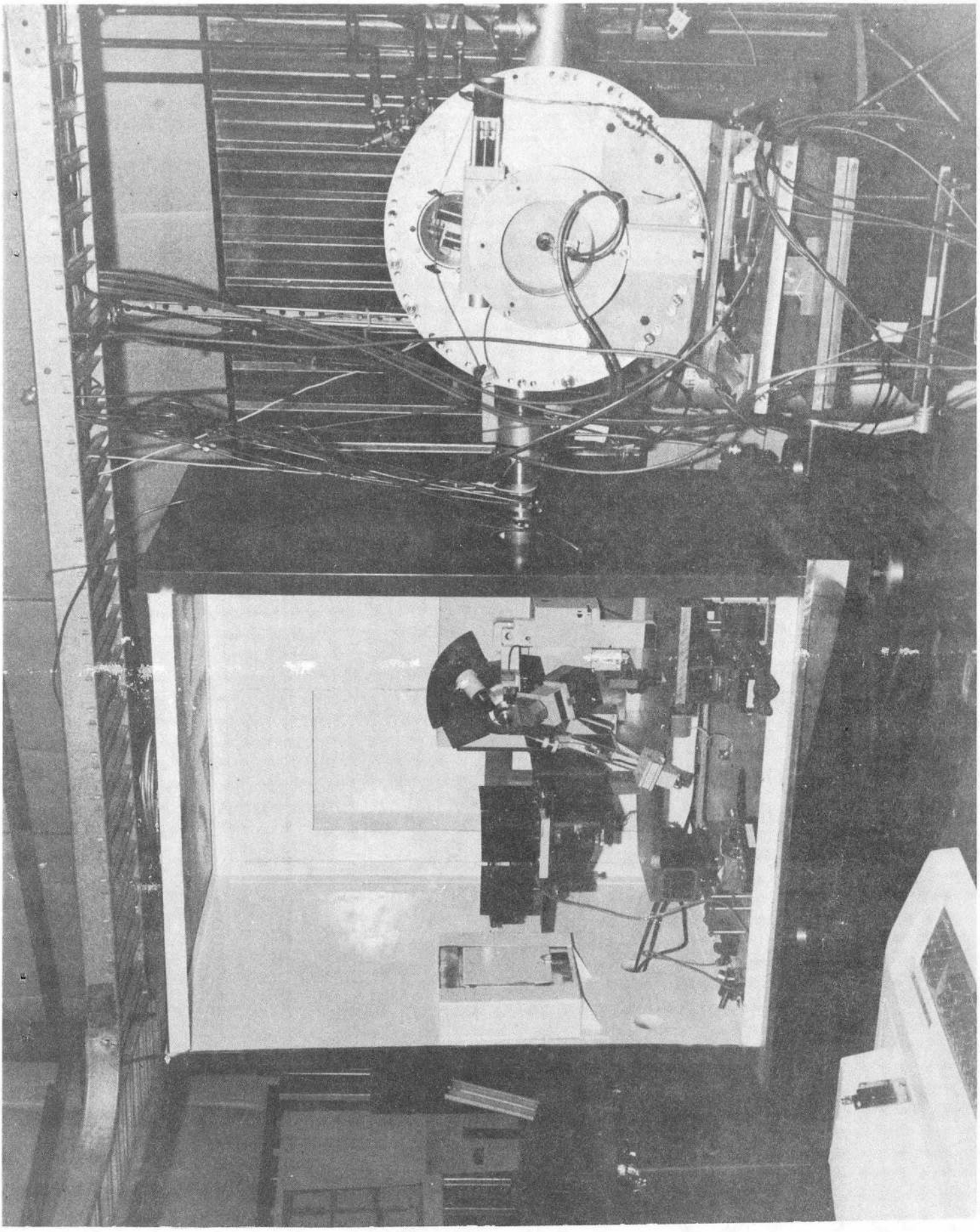

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Fig. 1

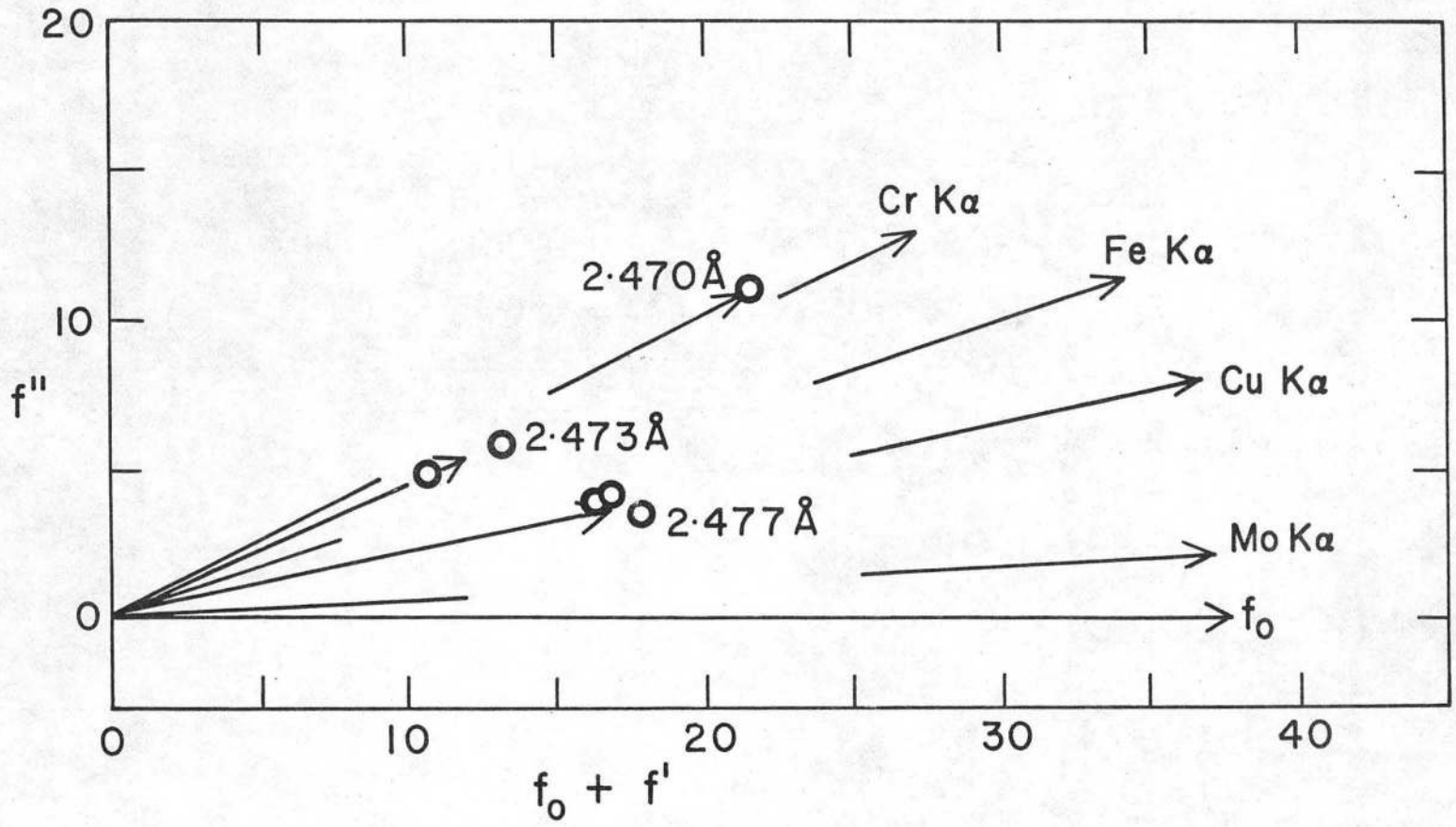

Fig. 2

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