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Author

Templeton, L.K.

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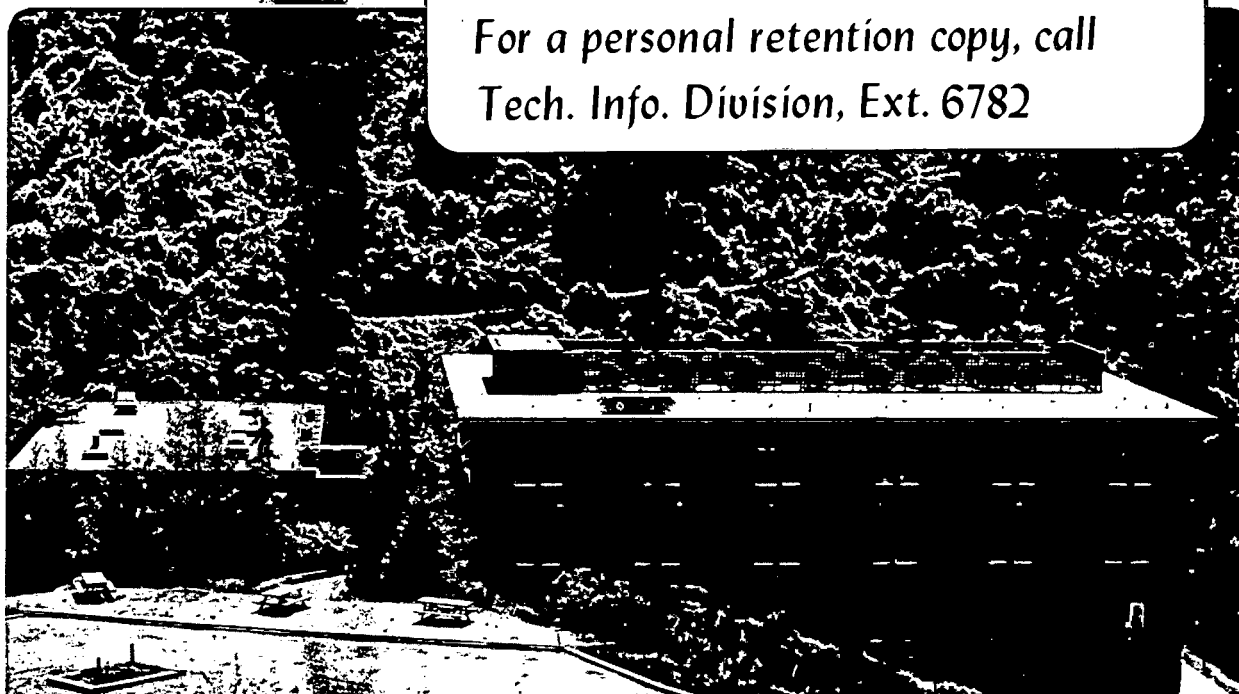
**L₃-EDGE ANOMALOUS SCATTERING BY GADOLINIUM AND
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SYNCHROTRON RADIATION**

Lieselotte K. Templeton, David H. Templeton,
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May 1981

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L₃-EDGE ANOMALOUS SCATTERING BY GADOLINIUM
AND SAMARIUM MEASURED AT HIGH RESOLUTION WITH
SYNCHROTRON RADIATION

Lieselotte K. Templeton and David H. Templeton

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California
Berkeley, California 94720 U.S.A.

R. Paul Phizackerley

Stanford Synchrotron Radiation Laboratory
Stanford, California 94305 U.S.A.

and Keith O. Hodgson

Department of Chemistry, Stanford University
Stanford, California 94305 U.S.A.

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ABSTRACT

The anomalous scattering terms f' and f'' for Gd and Sm near their L₃ absorption edges, measured in diffraction experiments with synchrotron radiation more nearly monochromatic than the natural level widths, show even larger effects than earlier measurements with a larger X-ray bandwidth. A test of angular dependence shows f' for Sm to decrease in magnitude with increasing diffraction angle, while f'' is essentially constant.

This work was supported by the National Science Foundation under Grant No. CHE-7919532 and the National Institutes of Health under Grant No. CA16748. The SSRL facilities are supported by the NSF under Contract DMR77-27489 in cooperation with the Department of Energy. The facilities at Lawrence Berkeley Laboratory are supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract W-7405-ENG-48.

INTRODUCTION

Anomalous X-ray scattering, a name for the effects of electronic energy levels on the phase and amplitude of scattered X-rays, is a powerful tool for solving diffraction problems. This is particularly true when synchrotron radiation is used, since its intense continuous spectrum permits the wavelength for a diffraction experiment to be chosen arbitrarily to high precision. The exceptionally large anomalous scattering effects which occur very near to the absorption edges can then be exploited. We have measured these effects in diffraction experiments with known crystals to provide a foundation for such applications, in particular to help solve the phase problem in macromolecular crystallography.

The largest effects we have measured occur near L_3 absorption edges of rare earth elements in the trivalent state. These edges span a range (2.26 Å for lanthanum to 1.34 Å for lutetium) which includes wavelengths often used for diffraction experiments. An earlier communication (Templeton, Templeton and Phizackerley, 1980) reported a study of praseodymium and samarium near their L_3 edges (2.08 Å and 1.85 Å) with values of f' as negative as -27.0 and -21.3 electrons/atoms and f'' as large as 27.3 and 23.3 e/atom. This work was done at the Stanford Synchrotron Radiation Laboratory with a focused beam line where the convergence of rays on the monochromator crystals resulted in an energy spread of about 6 or 8 eV. We then suspected, and have now confirmed, that even larger effects occur with more strictly monochromatic

radiation. Krause and Oliver (1979) give 3.60 eV for Pr, 3.86 eV for Sm and 4.01 eV for Gd as the natural widths* of the L_3 levels. These natural widths limit the sharpness of structure which can occur in the absorption spectra or in the curves for f' and f'' as a function of wavelength. The present paper reports a repetition of the samarium experiment and a study of the gadolinium L_3 edge (near 1.71 Å). Both experiments were carried out with unfocused radiation for which the energy spread was of the order of 1 eV. With this radiation the energy spread is not significant relative to the natural level widths.

*Full width at half maximum.

EXPERIMENTAL

The method (Templeton and Templeton, 1978) is to use a least-squares procedure to derive f' , f'' and a scale factor from diffraction intensities measured with a crystal of known structure, as in our previous studies with synchrotron radiation (Phillips, Templeton, Templeton and Hodgson, 1978; Templeton, Templeton and Phizackerley, 1980; Templeton, Templeton, Phillips and Hodgson, 1980). The modified Enraf-Nonius CAD-4 diffractometer described by Phillips, Cerino and Hodgson (1979) was used on the SSRL Beam Line I-5 where a channel-cut silicon crystal selects the wavelength. The radiation is reflected by the 220 plane on one side of the channel and then by the $\bar{2}\bar{2}0$ plane on the other side, resulting in an exit beam traveling in the same direction as the incident beam, but displaced vertically. The energy resolution, estimated as 1 eV at 10 keV, should be somewhat better at the energies near 7 keV used in this work. With the storage ring operating at an electron energy of 3.0 or 3.1 GeV and with an electron current between 50 and 80 mA there was ample intensity. In fact, attenuator foils (Cu or Ni) were used to avoid saturation of the scintillation detector by some of the stronger reflections. At this electron beam energy there is significant intensity due to the 2nd ($\lambda/2$) and perhaps even the 3rd ($\lambda/3$) harmonic radiation in the "monochromatic" X-ray beam. This $\lambda/2$ component was detected by measurement of reflections forbidden by the space group, which appeared to be present with intensities 20 to 30% of those of the corresponding $2h, 2k, 2l$ reflections when no pulse-height discrimination of the

scintillator signal was used.* With the normal discriminator settings this ratio was reduced to 2% or less, an amount which is considered acceptable for this experiment. This harmonic contamination was absent in the earlier work because the focusing mirror does not reflect wavelengths shorter than 1.2 or 1.3 Å.

We used crystals of sodium samarium ethylenediaminetetraacetate octahydrate ($\text{NaSmC}_{10}\text{H}_{12}\text{N}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$) and the isomorphous gadolinium salt which, like the same salts of many other rare earth elements, crystallize in the space group Fdd2 (Hoard, Lee and Lind, 1965). This samarium salt is the same one used by Koetzle and Hamilton (1975) in a study of anomalous neutron scattering. The determination of atomic coordinates and thermal parameters using other crystal specimens and Mo $K\alpha$ radiation ($R = 0.030$ for Sm and 0.024 for Gd) will be reported elsewhere.

Because the gadolinium experiment was our first chance to work at this high resolution, we chose to explore the absorption edge and white line with relatively short experiments at many closely-spaced wavelengths. Each of 46 reflections was measured twice at each wavelength with an $\omega-2\theta$ scan. The ω scan was 0.3° . The statistical accuracy required of the measurement was 3%. Measurements were rejected if too weak or too strong or if they failed the "not equal" test for forward and reverse scans. The $-16,2,0$ reflection was measured 12 times, and it was used to normalize the other intensities for beam variation because the

*The actual spectral content is something else, because different wavelengths have different probabilities for absorption and diffraction in the specimen crystal.

ion-chamber beam-monitor gave erratic results. The crystal had 12 faces including all members of the forms $\{111\}$, $\{1\bar{1}\bar{1}\}$, and $\{131\}$. Its volume was 0.0858 mm^3 . The value of μ ranged from 9.5 to 63 mm^{-1} and correction factors, calculated by our analytical absorption program, ranged from 8 to 648. The measurements included pairs of equivalent reflections which were averaged after this correction. This averaging resulted in sets of 21 to 27 independent data for which $(\sin\theta)/\lambda$ ranged from 0.20 to 0.47. We designate the two members of each Bijvoet pair as "independent".

The samarium experiment, performed 3 months later, used a crystal with the same morphology as the Gd crystal, except that the $\bar{1}\bar{1}1$ face was missing. Its volume was 0.0707 mm^3 . The value of μ ranged from 10 to 83 mm^{-1} , and correction factors for absorption were between 8 and 2300. In order to obtain better statistical accuracy we measured larger data sets at only four wavelengths. A number of reflections in the range $\theta = 5^\circ$ to 40° were measured using the "zigzag" mode and the same scan technique as in the Gd experiment. Some data were also taken up to $\theta = 64^\circ$ at 1.8448 \AA . The ion-chamber beam-monitor readings, which changed irregularly within each run by factors of as much as 2.8, were used to scale individual measurements. The reflection $-16,-2,0$, which was measured after each 300 sec of scan time, varied with standard deviations 2.4% to 6.9% after this scaling. Equivalent reflections and duplications were averaged, but few occurred except in the run at 1.8455 \AA . Most of the data consisted of Bijvoet pairs.

RESULTS AND DISCUSSION

The values of f' and f'' derived for gadolinium at 14 wavelengths are listed in Table I and plotted in Fig. 1. The width of the peak in the plot of f'' is about 0.001 Å or 4 eV. This width is equal to the natural level width within the experimental precision. Thus the values observed here are close to the limit which can be achieved with strictly monochromatic radiation. The relatively large standard deviations for some of the values may be explained by a combination of the small data sets and the instability of the beam intensity or variation of the wavelength; they all occur in a region where both f and μ are very sensitive to wavelength.

The results for samarium, based on the data taken below $\theta = 40^\circ$, are listed in Table II. They are plotted in Fig. 2 together with curves derived from an absorption spectrum of a powdered sample of the same salt measured with the same apparatus. After subtraction of a linear background for instrumental effects, the absorption spectrum was divided by λ and scaled to fit the high and low values of f'' to give the curve for f'' . This curve, extended with estimated values, was integrated by the Kramers-Kronig relation

$$f'(\omega) = \frac{2}{\pi} \int_0^{\infty} \frac{\omega' f''(\omega') d\omega'}{\omega^2 - \omega'^2}$$

over the interval from 1.93 to 1.54 Å. An empirical constant, -5.25 e/atom, was added to correct for the rest of the infinite interval, yielding the curve plotted for f' in Fig. 2. The fit of the two methods is gratifying. Again the width of the peak corresponds to the natural level width. The higher wavelength resolution has yielded extreme values differing by 5 e/atom for f'' and 10 e/atom for f' from those measured with the less monochromatic radiation of the focused beam (Templeton, Templeton and Phizackerley, 1980). Since measurements were made at larger diffraction angles in the earlier work, part of the difference in f' can be attributed to the angular dependence discussed below.

An important question about anomalous scattering is how f' and f'' vary with diffraction angle. Existing theoretical treatments predict changes of several percent, but the theory is incomplete and has been checked by rather few experiments. We are aware of no calculations of angular variation for edge resonances like those which dominate these rare-earth L-edge effects. To test the angular dependence in this samarium experiment we repeated the least-squares calculations with each data set divided according to angle into two parts. The additional data at 1.8448 Å provided sets for two additional angular intervals at that wavelength. Each data set covers a range of angles, but we associate each result with the mean value of $(\sin^2\theta)/\lambda^2$ for the n reflections. Since the angular variation must be an even function of θ , we expect its leading term to be linear in $\sin^2\theta$. The results, listed in Table III, uniformly indicate that the magnitude of f' decreases with increasing angle. For

1.8448 Å the trend is clear (Fig. 3), but at other wavelengths the change hardly exceeds the statistical accuracy because of the limited angular ranges. The values of f'' show no significant trend; each result is within one standard deviation of the average for that wavelength, and the trends at different wavelengths are evenly divided between an increase and a decrease. The four f'' points in Fig. 3 are best fitted by an increase with increasing angle, a result difficult to reconcile with theory. However, the effects are only a little above the statistical noise level. We suspect that some small systematic experimental error is affecting these results.

Wagenfeld (1975) has pointed out that when the angular dependence is calculated according to Honl's (1933) multipole expansion, it is not the same for different polarization components. This complication does not affect the analysis of the present experiment, because here the incident radiation is highly polarized and we are observing the σ component only. It may, however, affect a comparison of these results with experiments performed with unpolarized radiation or a different diffraction geometry.

We need not repeat here the method by which these anomalous scattering effects can be used to solve the phase problem. This subject has been discussed in several of the papers cited above, by Lye, Phillips, Kaplan, Doniach and Hodgson (1980), and by earlier authors referred to in these papers. The power for phase determination by measurements at several wavelengths is very dependent on the distances between points

representing f in the complex plane, as described by Phillips and Hodgson (1980) in calculations with data for cesium anomalous scattering. The present results, plotted in the complex plane and shown in Figs. 4 and 5, fall on loops with diameters about 24 e/atom. When each figure is combined with its reflection in the real axis (as when Bijvoet pairs are involved) the maximum distance between points in the direction of the complex axis is approximately 60 e/atom. We hope that these remarkable effects can soon be put to good use in the study of macromolecular structure. To accomplish this goal, an area detector data acquisition system is currently being developed at SSRL (Phizackerley, Cork, Hamlin, Nielsen, Vernon, Xuong and Perez-Mendez, 1980) which will be capable of rapidly measuring protein diffraction data at multiple wavelengths to high precision.

The crystals used in this work were grown by Helena W. Ruben. We thank her and Dr. Allan Zalkin for their cooperation in determining the structure of the samarium salt. This work was supported by the National Science Foundation under Grant No. CHE-7919532 and the National Institutes of Health under Grant No. CA16748. The SSRL facilities are supported by the NSF under Contract DMR77-27489 in cooperation with the Department of Energy. The facilities at Lawrence Berkeley Laboratory are supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. W-7405-Eng-48.

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Table I. Anomalous scattering terms for gadolinium near the L_3 absorption edge; n is the number of independent reflections, and the standard deviation of the last digit is shown in parentheses.

λ , Å	f'	f''	R, %	n
1.7071	-13.5(11)	8.7(10)	3.9	24
1.7086	-11.5(7)	10.8(11)	4.0	22
1.7095	-7.8(8)	14.9(12)	3.1	22
1.7098	-8.9(19)	19.9(31)	6.6	23
1.7100	-9.3(11)	29.8(22)	3.7	22
1.7101	-12.2(10)	31.2(30)	4.2	26
1.7103	-17.7(7)	28.7(19)	4.3	27
1.7104	-27.5(9)	29.8(15)	4.2	24
1.7106	-27.9(7)	27.6(12)	3.7	26
1.7107	-30.1(4)	20.9(4)	3.6	25
1.7109	-31.9(4)	16.1(4)	4.8	26
1.7112	-29.7(2)	10.5(3)	2.5	25
1.7117	-25.7(6)	7.3(6)	3.6	21
1.7136	-18.7(8)	5.5(9)	5.2	25

Table II. Anomalous scattering terms for samarium.

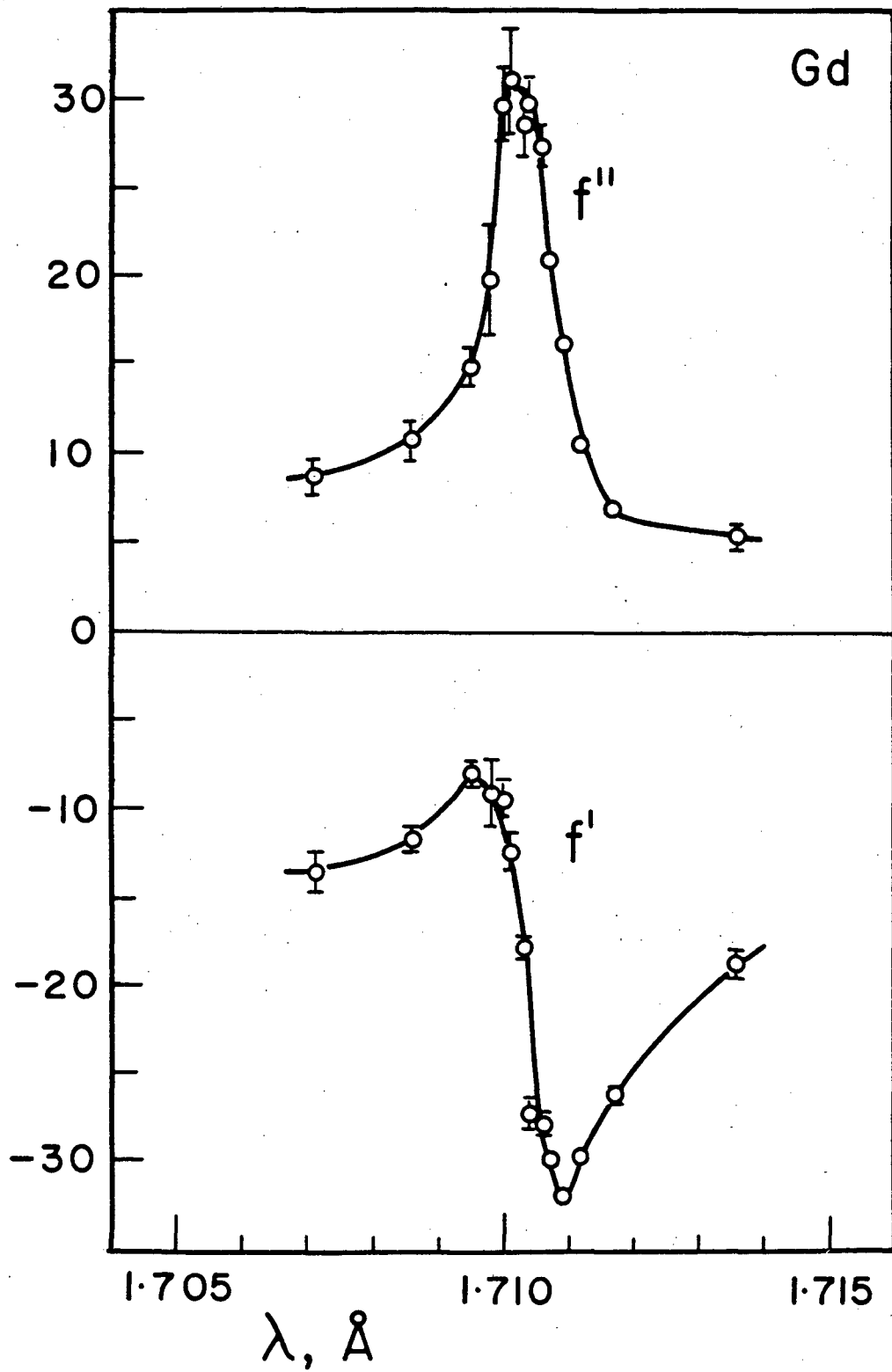
λ , Å	f'	f''	R, %	n
1.8443	-8.5(3)	21.2(3)	6.7	730
1.8448	-17.8(3)	28.8(3)	7.1	727
1.8455	-31.5(1)	17.9(1)	5.2	724
1.8489	-19.5(2)	4.4(2)	4.6	451

Table III. Angular dependence of f' and f'' for samarium. Listed under $(\sin^2\theta)/\lambda^2$ are its mean value for each set of n reflections.

λ	f'	f''	R, %	n	$\frac{\sin^2\theta}{\lambda^2}$
1.8443	-8.5(4)	21.8(5)	6.5	383	0.0482
1.8443	-7.9(6)	20.8(6)	6.9	347	0.1007
1.8448	-18.0(4)	29.1(5)	6.8	382	0.0482
1.8448	-17.3(6)	29.3(5)	7.1	345	0.1006
1.8448	-16.9(4)	30.0(4)	5.1	408	0.1540
1.8448	-15.6(4)	29.5(4)	4.0	428	0.2117
1.8455	-31.7(2)	17.9(2)	5.2	382	0.0483
1.8455	-31.4(2)	18.2(2)	5.1	342	0.1005
1.8489	-19.7(2)	4.5(2)	4.5	328	0.0485
1.8489	-19.3(3)	4.2(4)	4.8	123	0.0876

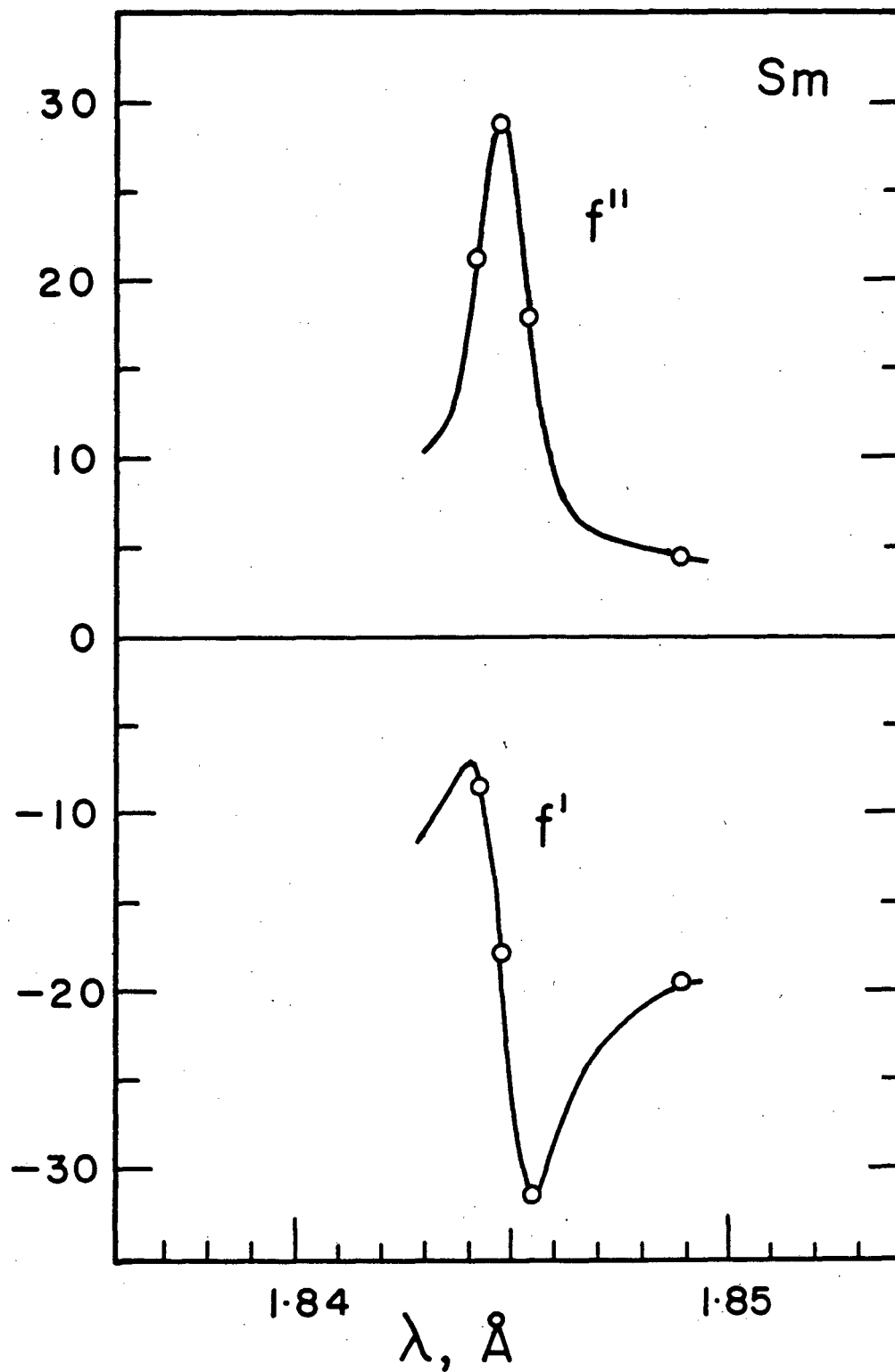
FIGURE CAPTIONS

- Fig. 1. Anomalous scattering terms f' and f'' for gadolinium near the L_3 edge.
- Fig. 2. Anomalous scattering terms f' and f'' for samarium near the L_3 edge. The points are results of the diffraction experiment; the curves are derived from the absorption spectrum as described in the text.
- Fig. 3. Dependence of f' and f'' on diffraction angle for Sm at 1.8448 Å. Vertical error bars indicate standard deviations from least squares. Horizontal error bars indicate σ of the distribution of $(\sin^2\theta)/\lambda^2$ for each data set.
- Fig. 4. Plot in the complex plane of $f' + if''$ for gadolinium near the L_3 edge.
- Fig. 5. Plot in the complex plane of $f' + if''$ for samarium near the L_3 edge. The curve corresponds to the calculated curves of Fig. 2.



XBL 808-10924

Fig. 1



XBL 808-11073

Fig. 2

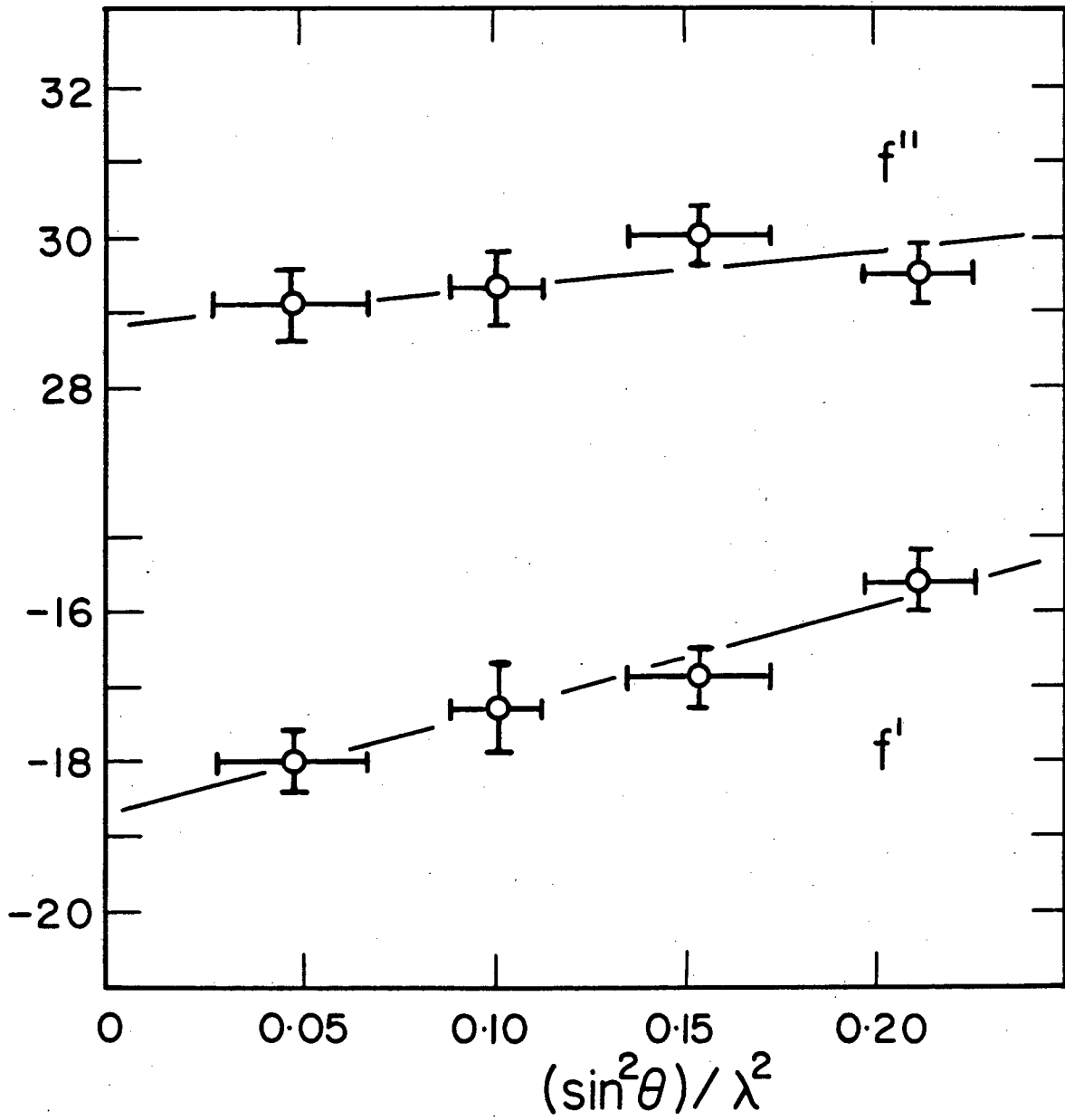


Fig. 3

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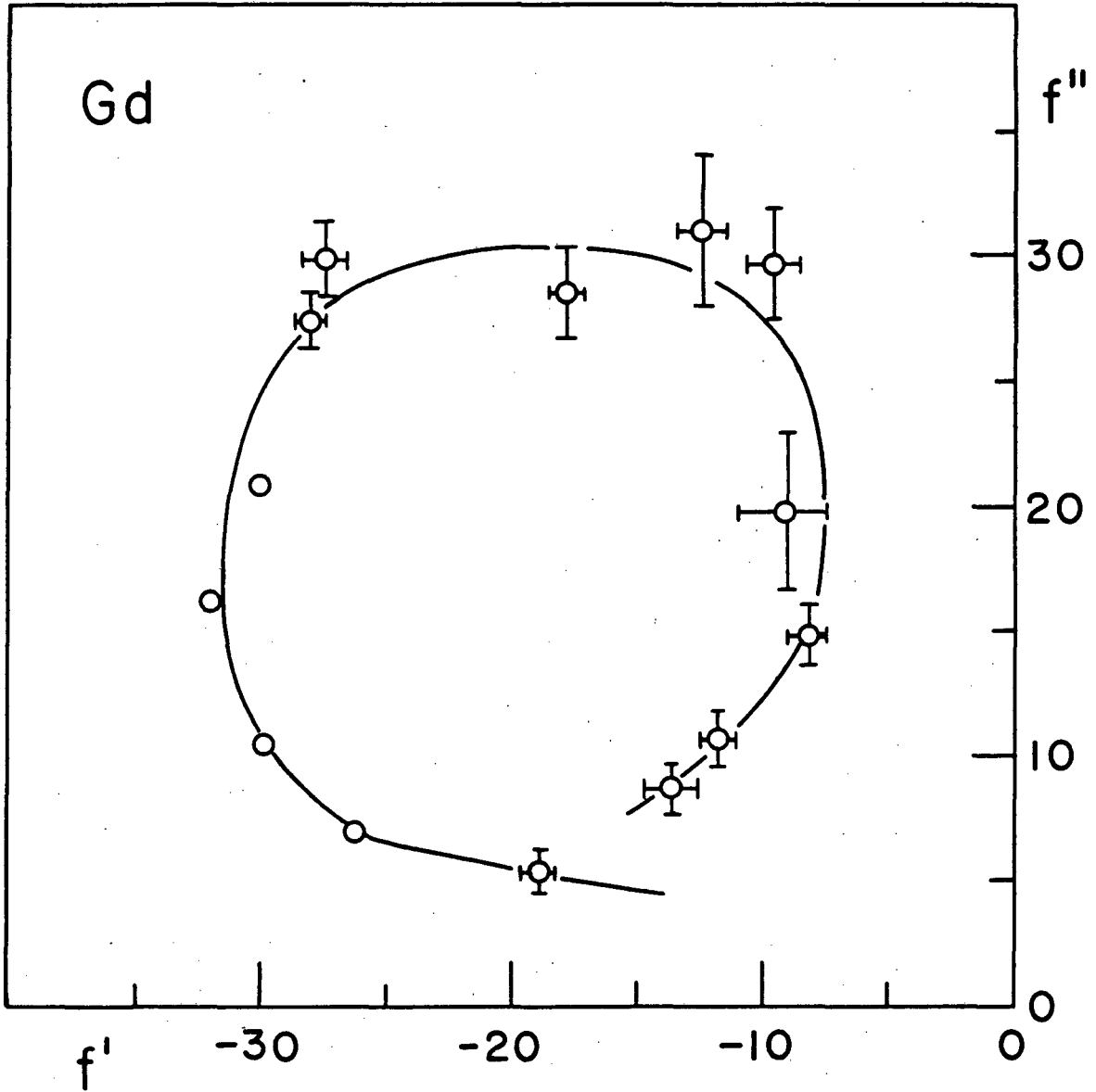


Fig. 4

XBL 808-11072

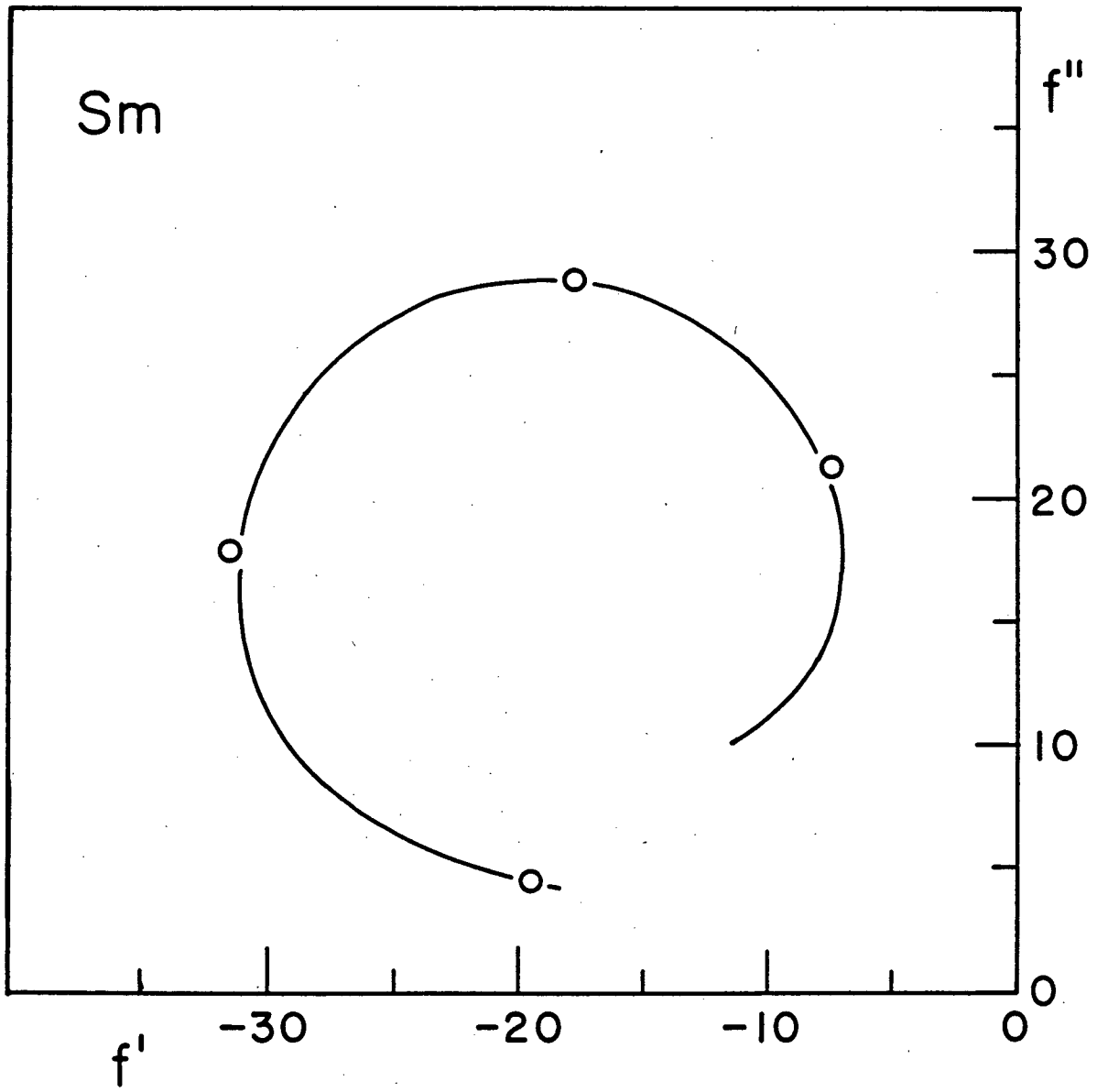


Fig. 5

XBL 808-10925

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