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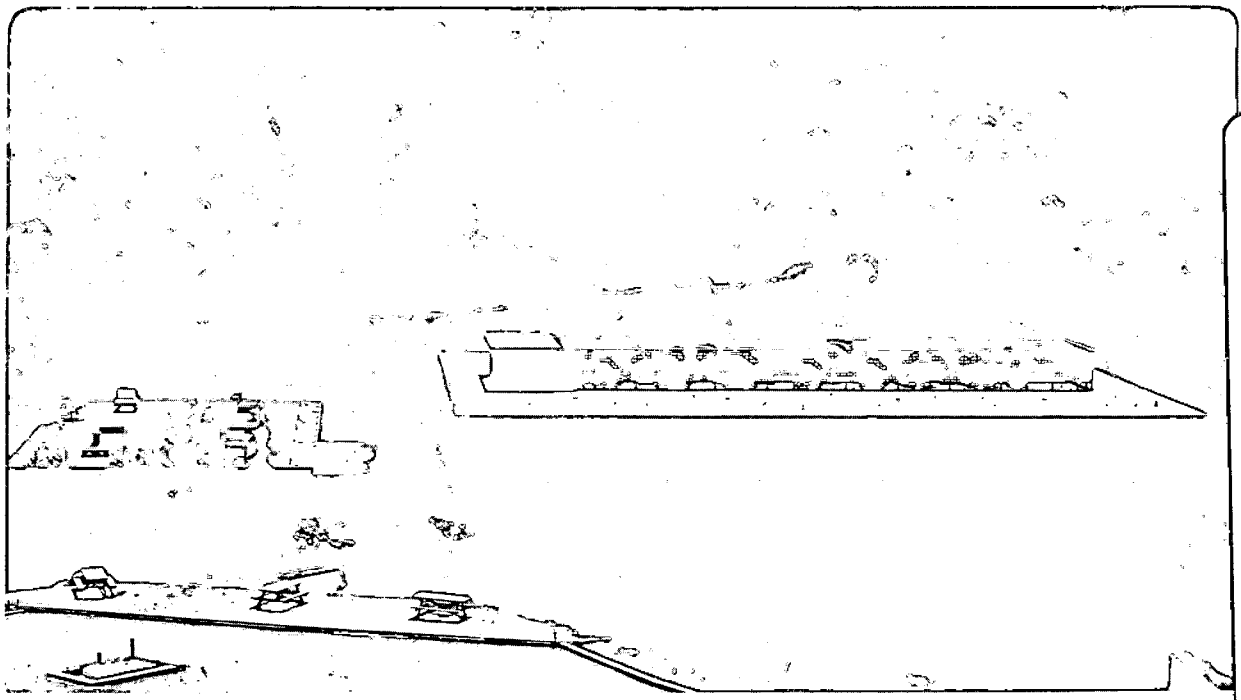

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IN SITU XANES OF AN IRON PORPHYRIN IRREVERSIBLY ADSORBED ON AN ELECTRODE SURFACE

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ABSTRACT

In situ iron K-edge X-ray Absorption Near Edge Structure, XANES, has been employed to examine the axial coordination of μ-oxobis [iron mesotetrakis (methoxyphenyl) porphyrin] $(FeTMPF)_20$, irreversibly adsorbed on a high area carbon substrate, Black Pearl (BP), as a function of the applied potential. Analysis of the XANES provides conclusive evidence that the coordination about $Fe(3^+)$ in the supported, fully oxidized macrocycle is remarkably different from that about $Fe(^{2+})$ in the corresponding fully-reduced macrocycle. In the adsorbed, oxidized state, $(FeTMPP)_20$ retains its μoxo character and it undergoes a two-electron reduction to yield predominantly four-coordinate square planar FeTMPP without axial ligation.

INTRODUCTION

The adsorption of a variety of atomic and molecular species on electrode surfaces has been found to promote the rates of a growing number of electron transfer processes of fundamental and technological importance.[1] Essential to the further elucidation of the factors underlying this phenomenon is a better understanding of the changes in the electronic and structural characteristics of these species induced by the binding to the surface and by variations in the externally applied potential.

The rather recent advent of synchrotron radiation has opened new prospects for the development and implementation of in situ methods involving atomic adsorption on single crystal substrates,[3] applications of these techniques to the in situ study of molecules adsorbed at monolayer coverages on electrode surfaces have been very limited.[4] This may be attributed, in part, to the relatively small number of molecules that can be accommodated on a nominally smooth surface even at saturation coverages (ca.10^{-10} to 10^{-11} mol·cm^{-2}), a factor that makes detection exceedingly difficult. Low-Z, high area supports, such as carbon, afford a convenient means of increasing the number of molecules exposed to the X-ray beam without introducing large losses due to radiation attenuation. In fact, this strategy has been used with much success in in situ studies involving ^{57}Fe Mossbauer-effect spectroscopy.[5] Besides its relative transparency to high energy radiation and high electronic conductivity, the advantages of carbon over other kinds of supports are two-fold: It displays high affinity for a variety of molecular species, and it exhibits little or no activity for many electrochemical processes of interest.

This communication presents in situ iron K-edge X-ray Adsorption Near Edge Structure, XANES, spectra for μ-oxobis[iron meso-tetrakis (metroxyphenyl) porphyrin], $(FeTMPP)_20$, irreversibly adsorbed on Black Pearl (BP), a high area carbon with about 1000 m^2.g^{-1}, in

aqueous electrolytes. Some of the properties of this specific adsorbate-substrate system have been investigated with in situ ^{57}Fe Mossbauer-effect spectroscopy.[5] The information derived from the Fe XANES experiments described herein complements the previous Mossbauer results and, most importantly, provides conclusive evidence regarding the modifications in axial coordination and oxidation state of iron associated with the surface-bound redox process.

EXPERIMENTAL

$(FeTMPP)_2O$ was synthesized and purified according to procedures specified in detail elsewhere,[6] and tetracoordinated-planar iron(2+) phthalocyanine (FePc) was obtained from Eastman Kodak and purified by sublimation at reduced pressures (ca. 10^{-2} torr). The adsorption of $(FeTMMP)_2O$ on the carbon surface was effected from dichloromethane solutions as described in a previous communication.[5] The electrochemical properties of the highly dispersed material were examined by mixing the dry $(FeTMPP)_2O$/BP with an aqueous Teflon emulsion until the material acquired some degree of elasticity. Larger and better defined voltammetric peaks were always observed by keeping the mixtures moist (adding distilled water if necessary) during preparation and storage.

For the electrochemical measurements, a small amount of Teflon-bonded $(FeTMPP)_2O$/BP was applied onto the surface of a slightly receded Tacussel solid carbon disk electrode (ca. 1 mm diameter) used for rotating disk experiments. Voltammetric measurements were performed in various electrolytes using a gold counter electrode, a saturated calomel reference electrode, SCE, and a Pine RDE-4 potentiostat/Yokowaga XY recorder system.

Iron K-edge XANES spectra were acquired at the National Synchrotron Light Source, NSLS, at Brookhaven National Laboratory (Line X-1OC). All experiments were conducted in the fluorescence mode with a cell shown schematically in Figure 1, using a Mn filter

interposed between the electrode and a pin-diode detector. A standard ion chamber with flowing nitrogen was used to measure the incident X-ray intensity, I_O. The electrode consisted of a piece of pyrolytic graphite (2 mm × 2 mm × 15 mm) cast in Kel-F attached to a Teflon stem that enabled both rotation and translation along an axis perpendicular to cell window. With this arrangement the entire X-ray beam could be focused onto the electrode surface. With 0.3 mm slits, effective spectral resolution (i.e., the convolution of the total energy bandwidth of the Si<111> monochromator and the Fe-K-edge core-hole linewidth) was estimated to be 2.0 eV at 7,110 eV. Harmonic rejection was accomplished with a post-monochromator mirror.[7] XANES data were obtained with a step size of 0.2 eV/point; normalization and differentiation were performed as described elsewhere.[8] The energy calibration of each data set was maintained by use of an iron foil reference. The energy of the first inflection point in the first differential XANES for the iron foil was set to 7110.0 eV.

The Teflon/$(FeTMPP)_2O$/BP carbon paste was applied onto a thin, shallow groove carved along the long axis of the graphite piece. Immediately after the cell was assembled and the electrolyte was deaerated, a series of voltammetry curves were recorded with the electrode well removed from the window until features associated with the redox process could be clearly identified. During data collection, the electrode was pressed firmly against the thin polyethylene sheet (10-13 μm) attached to the back side of the Kapton tape window to avoid contact of the carbon with the adhesive backing. After the initial spectra were acquired, the potential was scanned to the desired value at very small rates to avoid large capacitive (and pseudocapacitive) currents without disturbing the overall geometry. Despite the large distortions associated with the highly non-uniform current distribution, due primarily to IR drop, clear voltammetric peaks could be observed in every instance provided the potential excursion was sufficiently wide. Iron XANES spectra were recorded with the

$(FeTMPP)_2O$ in the fully oxidized and fully reduced state and, in some cases, with the electrode polarized at the redox peak potential (as determined from the undistorted voltammogram) at which both species were present in equal amounts.

RESULTS

Electrochemical Aspects. The cyclic voltammetry of $(FeTMPP)_2O$/BP in 0.1 M NaOH, shown in Fig. 2, was found to display a characteristic redox peak centered at about -0.72 V vs SCE.[5] Because of the uncertainties associated with the precise amount of material applied to the electrode surface (on the order of a few mgs), it is not possible to determine whether all or only a fraction of the macrocycle is electrochemically active from analysis of a single voltammogram. Some evidence that the fraction of active material is independent of the coverage was obtained by analyzing voltammetry curves for $(FeTMPP)_2O$/BP mixtures containing different macrocycle-to-carbon ratios. As determined from these data, plots of the charge under the redox peak normalized by the capacitive current measured at a potential away from the redox feature versus the fraction of macrocycle in the mixture were found to be linear in the range between 4 to 40% $(FeTMPP)_2O$. This test is not definitive, since the capacitive current away from the redox peak would be proportional to the amount of carbon in the sample if and only if the interfacial capacity of the latter is not influenced by the presence of the adsorbate. However, as discussed below, the effect of electrode potential on the XANES data indicated that essentially all of the adsorbed macrocycle was electrochemically active.

Voltammetric measures as a function of pH were found to yield similar curves to those reported by Shigehara and Anson for coatings of FeTPPC1 on ordinary pyrolytic graphite electrodes.[9] In accordance with these authors, the otherwise clearly identifiable redox peaks observed under strongly acidic and strongly basic conditions became broad and ill-defined at close to neutral pH values.

XANES Data. The in situ K-edge X-ray adsorption spectrum of 40% $(FeTMPP)_20/BP$ in 0.1 M NaOH in the oxidized state (Figure 3, middle curve) is clearly different to that of the parent macrocycle in crystalline form (Figure 3, top curve). The differential spectra of the latter, however, shown in Figure 4 (top curve), are very similar to those of the closely related crystalline macrocycle μ-oxobis[iron meso-tetrakis(phenyl)porphyrin], $(FeTPP)_20$, reported by other workers.[10] The pre-edge peaks at 7112.5 and 7112.4 eV for crystalline $(FeTMPP)_20$ and $(FeTMPP)_20/BP$, respectively, are well known and sensitive indicators of the site symmetry about iron. They are due to electronic transitions from the iron $1s \rightarrow 3d$ peaks for the crystalline (0.115) and adsorbed (0.093) $(FeTMPP)_20$ on BP are consistent with those known for five-coordinate μ-oxo-bridged (Fe(3+) macrocycles.[12-14] Inspection of the XANES (Figure 3) and first differential XANES (Figure 4) reveals a diminution of the pre-edge peak and an alteration of the edge peak of crystalline $(FeTMPP)_20$ upon adsorption of the macrocycle on the surface and subsequent exposure to the electrolyte. These effects are most obvious in the first differential XANES (Figure 4, of top and middle curves) upon comparison of the widths and shapes of the peaks at ca. 7122 eV and the intensities of the peaks at 7111.0 eV, which are the edge and pre-edge peak inflection points, respectively. Furthermore, the inflection points at ca. 7128 and 7135 eV in the first differential XANES for crystalline $(FeTMPP)_20$ are not resolved in those data for adsorbed $(FeTMPP)_20$ (Figure 4). These differences may be ascribed to a molecular relaxation induced by the removal of the macrocycle from its original crystal lattice, a process that could generate a multiplicity of closely related iron environments (...Fe(3+)-0-Fe(3+)...) and thus lead to a global broadening alteration of the XANES. This explanation is in agreement with the observation of marked

losses in the recoiless fraction for the same material in similar environments for which no ^{57}Fe Mossbauer-effect spectra could be observed at room temperature even in the absence of electrolyte.[5]

Pronounced changes in the iron XANES were observed (Figure 3, bottom curve) upon polarizing the electrode at a potential negative enough for the adsorbed macrocycle to undergo complete reduction. Most prominent is the disappearance of the pre-edge peak at 7112.4 eV for the oxidized macrocycle and the shift in the onset of the absorption edge with the appearance of a new, incompletely-resolved pre-edge peak at ca. 7116 eV. This first differential XANES (Figure 4, bottom curve) reveals two strong peaks at 7114.3 and 7121.5 eV, corresponding to the pre-edge and edge inflection points, respectively. The presence of this pre-edge peak for the fully-reduced, supported macrocycle is typical of a four-coordinate, square planar environment iron. Such pre-edge peaks are characteristic of four-coordinate square planar complexes of Fe(2+)[11], such as for iron mesotetrakis (phenyl)porphyrin, as well as for those of Cu(1+)[15] and Ni(2+).[16] Any analogy with previous assignments, [15,16] the pre-edge peak observed for the reduced FeTMPP/BP complex is due to an electronic transition from the iron $1\underline{s}$ orbital to an empty 4_{pz} orbital.

The XANES and first differential XANES for iron (2+) phthalocyanine (with four-coordinate, square planar Fe-N ligation and no axial ligation) are shown in Figures 5 and 6, respectively. Note the well-resolved pre-edge peak at 7116.6 eV with an inflection point energy of 7115.0 eV. Comparison of these data (Figures 5 and 6) with those for the reduced, adsorbed porphyrin (Figures 3 and 4, bottom curves) reveals one important similarity, namely, the presence of pre-edge peaks of nearly equal magnitude at about 7116 eV, which are characteristic of Fe(2+) four coordinate square planar geometry. The apparent resolution of the pre-edge peak (due to a $1\underline{s} \rightarrow 4\underline{pz}$ electronic transition) for the reduced, adsorbed

macrocycle is clearly less than that for either crystalline FePc (recorded under the same experimental conditions) or iron meso-tetrakis(phenyl)-porphyrin.[10] There are at least two plausible explanations for this effect: (i) a multiplicity of closely related iron environments (all with four-fold square planar coordination) due to structural distortions of the TMPP framework upon adsorption and reduction of the parent macrocycle, and; (ii) a heterogeneity of coordination, such that the principal fraction of iron in the reduced, adsorbed macrocycle is four-coordinate square planar and a small fraction is five- or six-coordinate with axial ligands. Nevertheless, upon polarizing the electrode at a potential positive enough to reoxidize the adsorbed FeTMPP, the XANES data obtained were essentially identical to those shown in Figure 3 (middle curve) for the fully oxidized $(FeTMPP)_2O$/BP complex. This indicates that, to the level of sensitivity of the measurements, the redox process is completely reversible. It is remarkable that such a complex molecular rearrangement between the oxidized and reduced forms is so reversible.

CONCLUSIONS

The <u>in situ</u> iron XANES described herein provides conclusive evidence, for the first time, that the coordination about Fe(2+) in the supported, fully-reduced macrocycle is remarkably different from that about Fe(3+) in the corresponding fully oxidized macrocycle. It is thus concluded from the iron K-edge XANES results that $(FeTMPP)_2O$ in the adsorbed state retains its μ-oxo character and undergoes a two-electron reduction to yield predominantly axially-uncoordinated FeTMPP. This assignment is in agreement with earlier in-situ ^{57}Fe Mossbauer-effect measurements on the same system in which the isomer shift and quadrupole splitting of the reduced species observed at about 250 K were consistent with those of a ferrous porphyrin species.[5] As was demonstrated elsewhere,[5] the potential drop across high-area-carbon/electrolyte interfaces does not seem to be affected by freezing and

electrolyte while maintaining the electrode under potential control. Under these conditions, it might become possible, for example, to expose the reduced form of the macrocycle to reactive gases such as dioxygen and, provided the temperature is low enough, stabilize otherwise highly reactive adducts. This strategy is now being examined; should it prove successful, it would open new prospects for the close examination of electronic and structural aspects of reaction intermediates of macrocycle-mediated electrocatalytic processes.

ACKNOWLEDGMENTS

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LIST OF FIGURES

Figure 1. Schematic diagram of the electrochemical cell used for the in situ XANES measurements.

Figure 2. Cyclic voltammetry of 40%w/w$(FeTMPP)_2O$/BP in 0.1 M NaOH aqueous solution. Scan Rate: 5 $mV\text{-}s^{-1}$.

Figure 3. Normalized iron K-edge fluorescence XANES data: top curve, microcrystalline $(FeTMPP)_2O$ powder with five-coordinate μ-oxo bridging ligation of Fe(3+) atoms; middle curve 40% $(FeTMPP)_2O$/BP in 0.1 M NaOH in the original oxidized state, -0.43 V vs. SCE; bottom curve, 40% $(FeTMPP)_2O$/BP in 0.1 M NaOH in the reduced state, -0.90 V vs. SCE. The Vertical scale is offset for clarity.

Figure 4. First differential iron XANES of the data shown in Figure 3. The order of the curves is the same as that identified in the caption to Figure 3. Vertical scale is offset for clarity.

Figure 5. Normalized iron K-edge fluorescence XANES data for microcrystalline (phthalocyaninato)iron(II) powder with four-coordinate, square planar Fe-N ligation of Fe(2+), i.e. no axial ligands.

Figure 6. First differential iron XANES of the data shown in Figure 5 for (phthalocyaninato)iron(II).

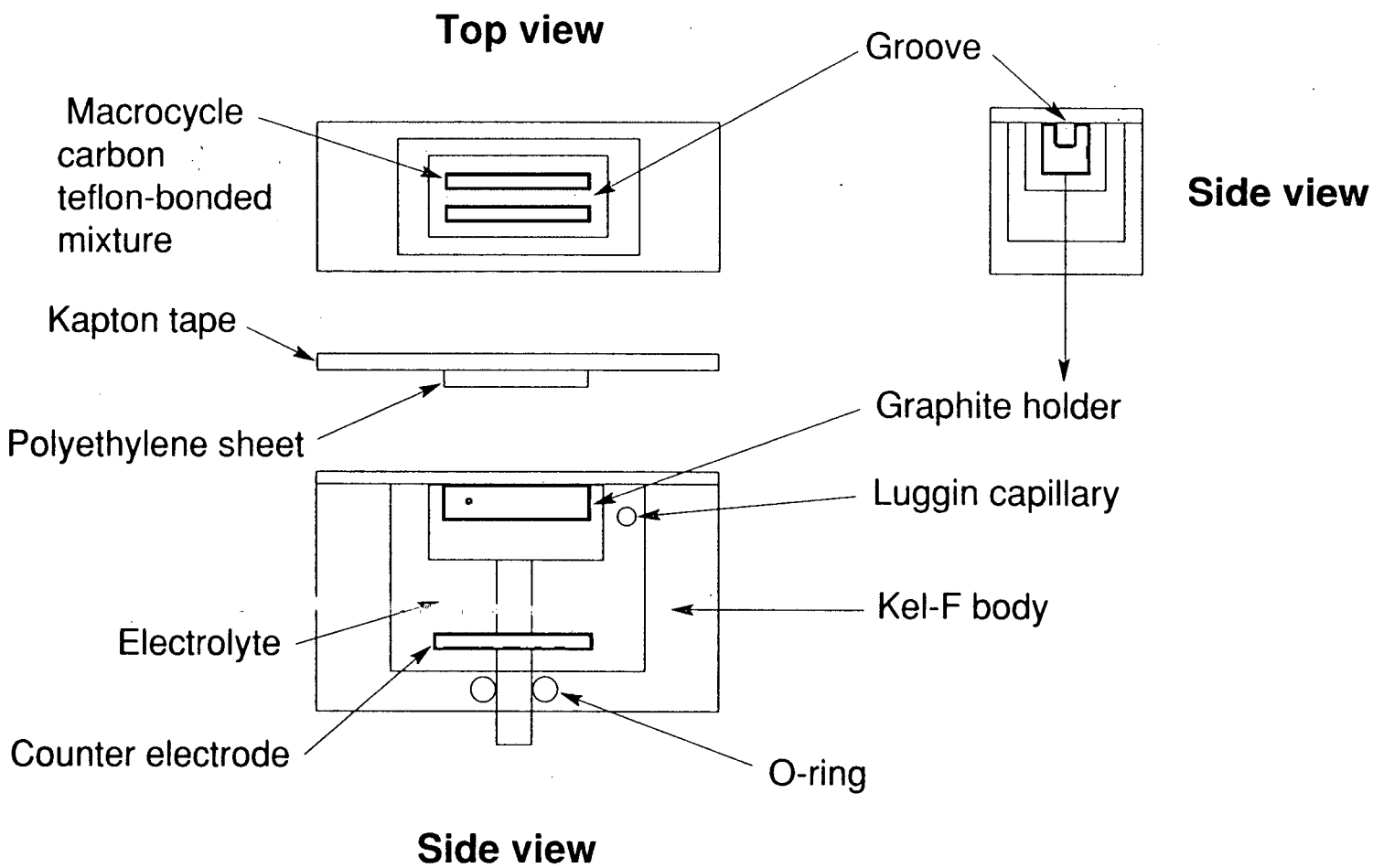

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FIGURE 1

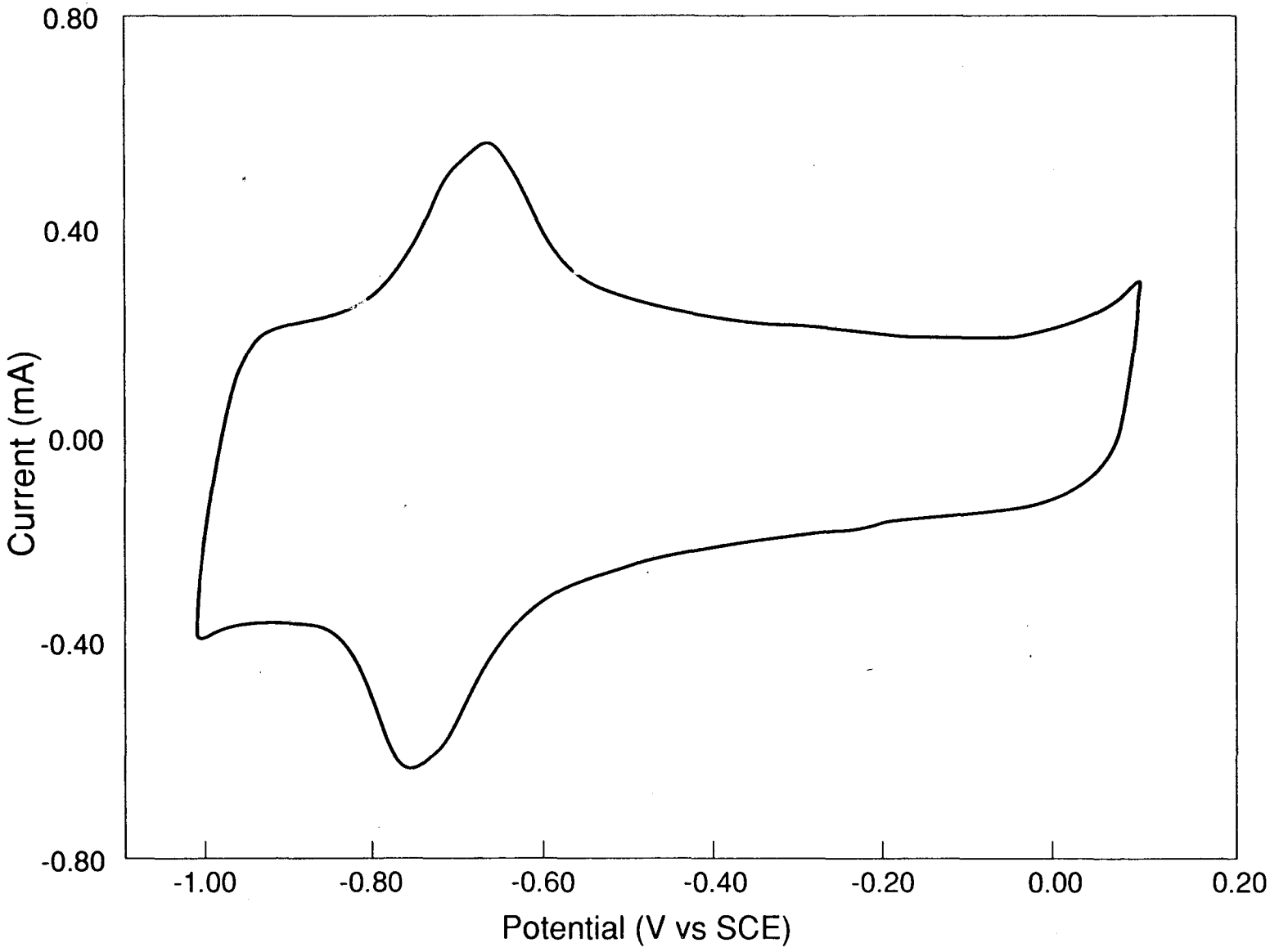

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FIGURE 2

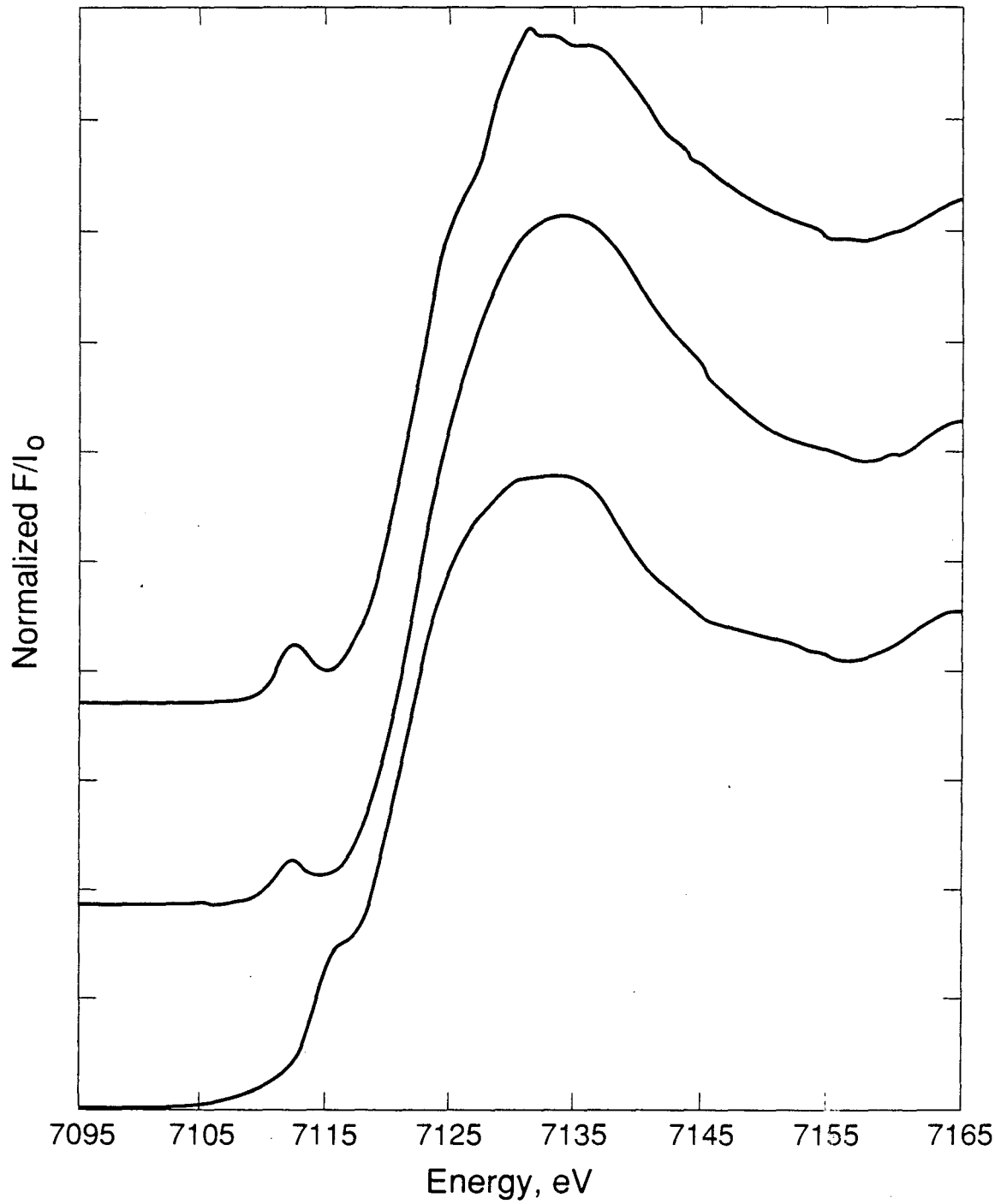

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FIGURE 3

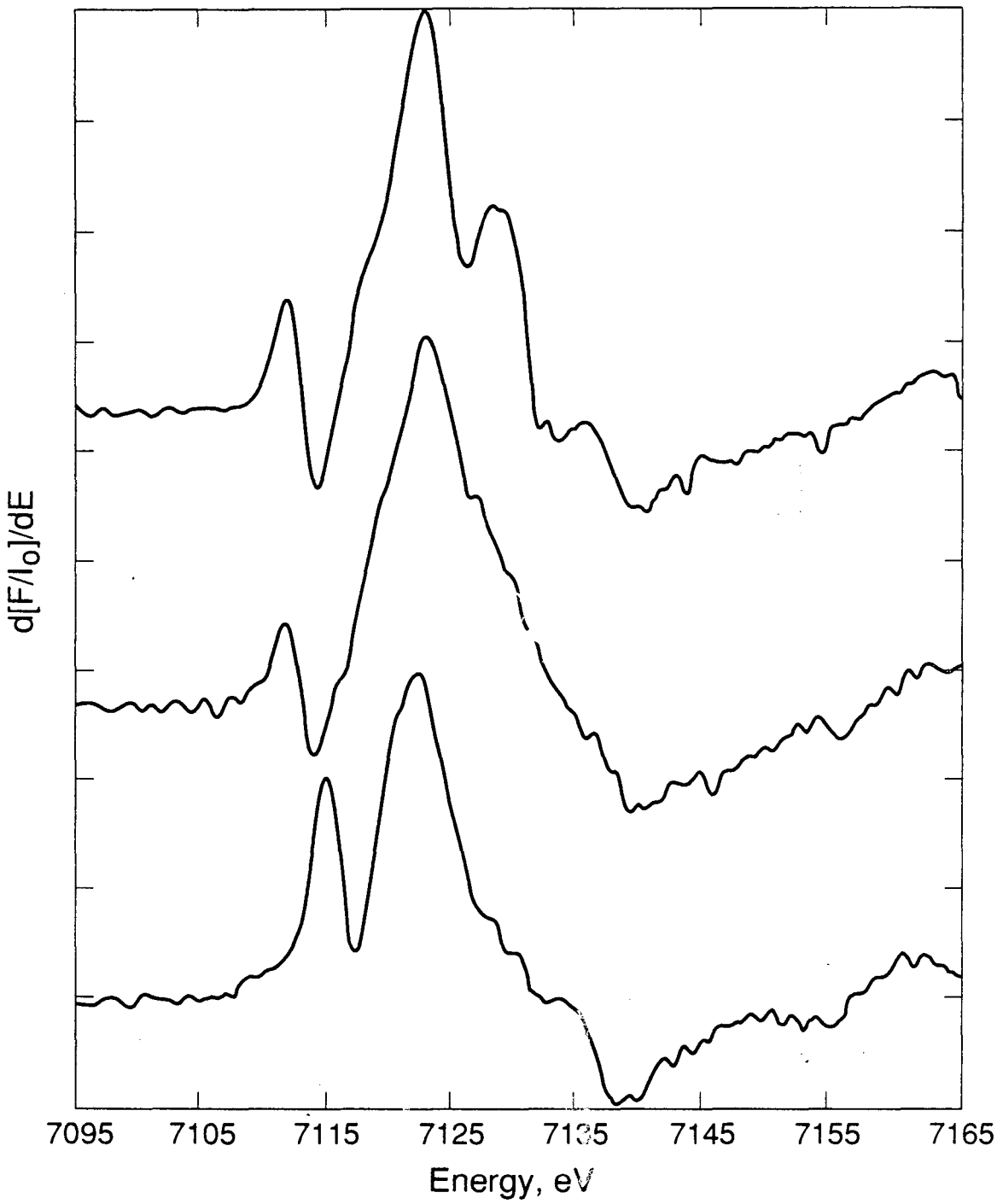

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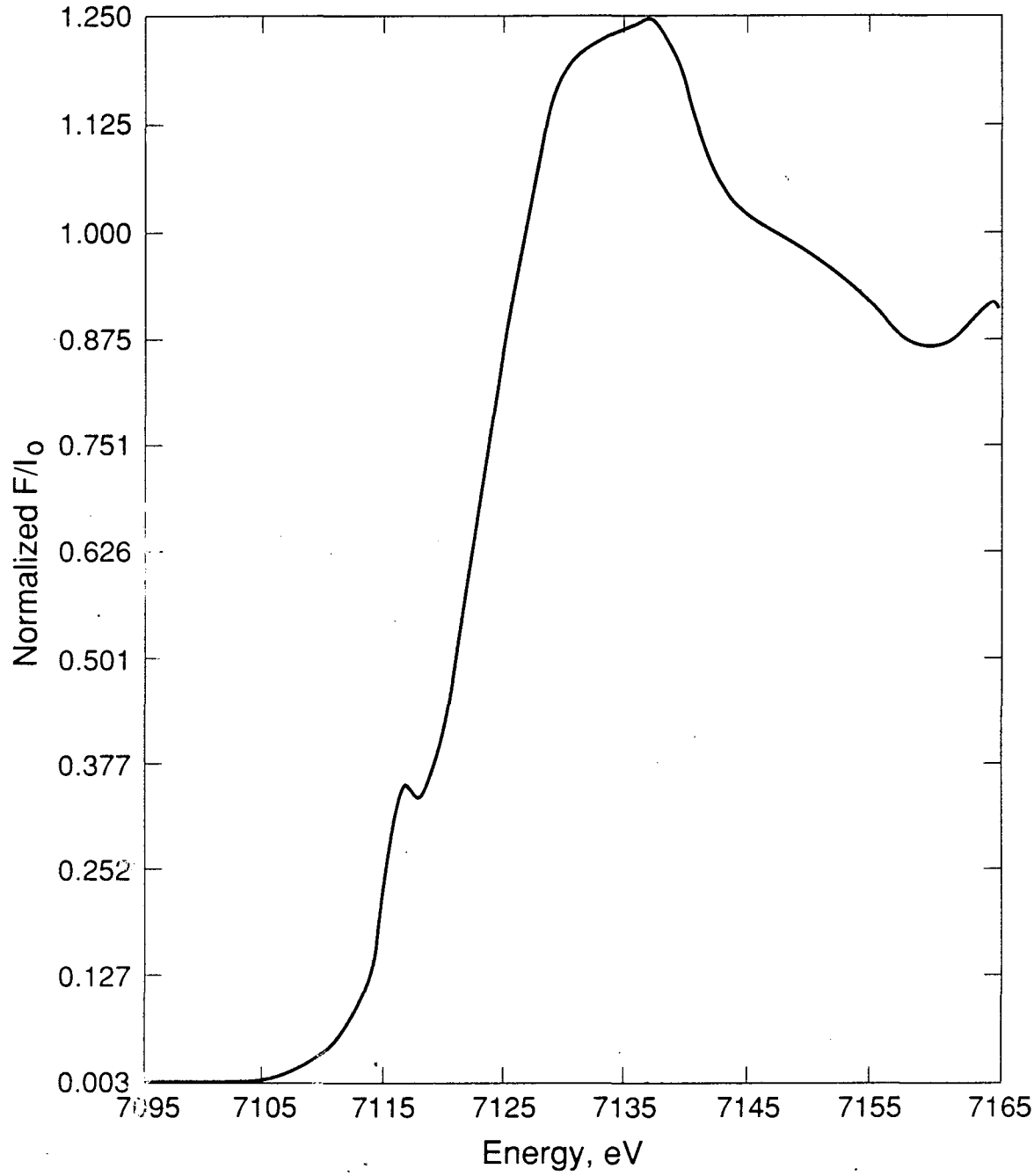
FIGURE 4



XBL 912-6037

FIGURE 5

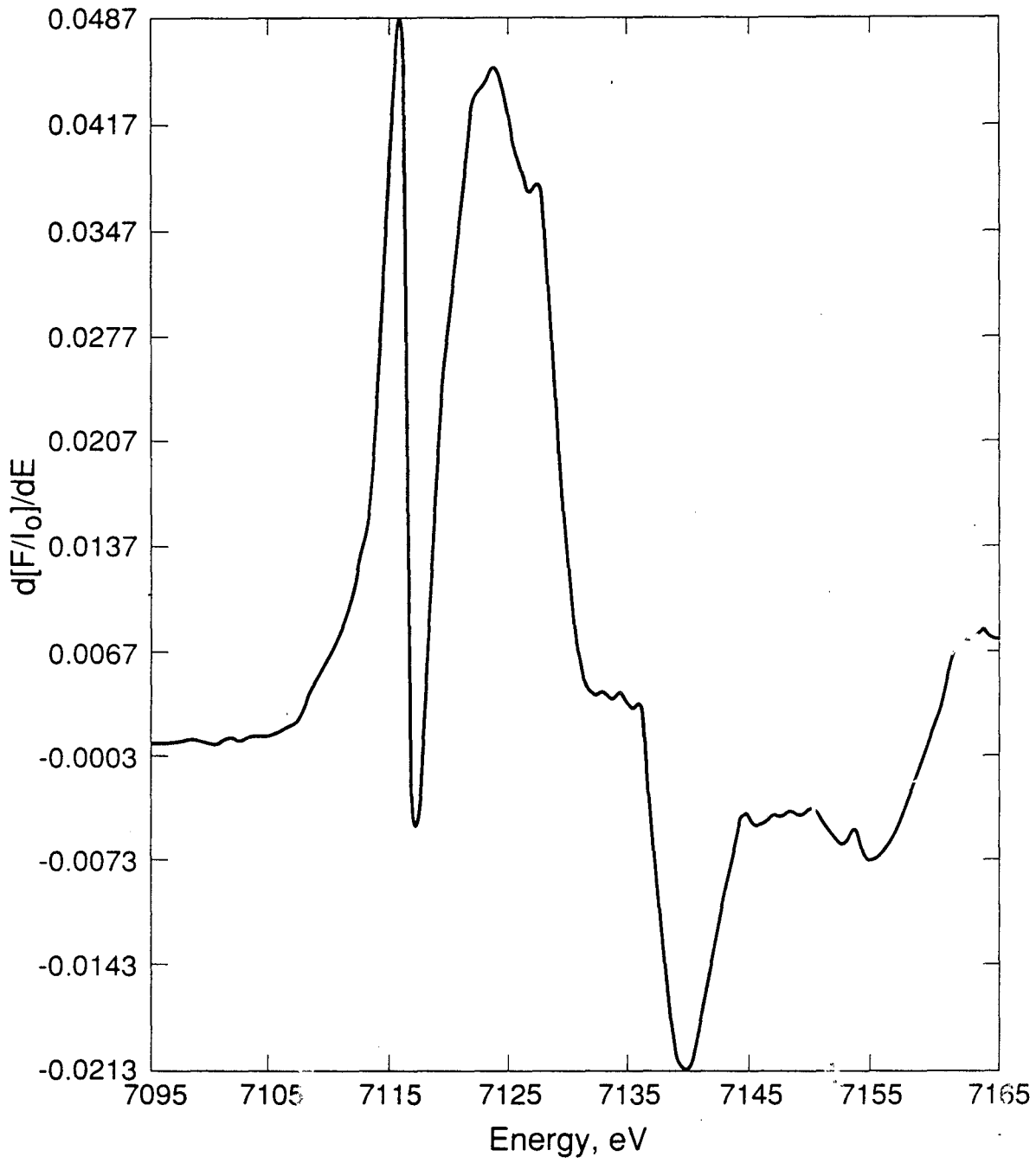


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FIGURE 6

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