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FINAL TECHNICAL REPORT

A Study of X-Ray Absorption Edge Spectroscopy
As a Tool for Solid-State Chemical Research

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A STUDY OF X-RAY ABSORPTION EDGE SPECTROSCOPY
AS A TOOL FOR SOLID-STATE CHEMICAL RESEARCH

Contract No. Nonr 4463(00)

Final Technical Report

The following final technical report describes progress made on Contract Nonr 4463(00), "A Study of X-Ray Absorption Edge Spectroscopy as a Tool for Solid-State Chemical Research," for the duration of the contract, February 1, 1964 to January 31, 1966.

PROBLEM STATEMENT

Interpretation of the properties of solids often rests on an assumption concerning valence and bond type of the component atoms. The word "assumption" is used since a direct determination of parameters such as valence is normally not available. We are seeking to evaluate the usefulness of x-ray absorption edge spectroscopy as a research tool to satisfy this need for direct determination of valence, bond type, and coordination.

Our method of attack is to obtain background spectra of atoms in well-defined states in order to allow comparison with spectra obtained on compounds of interest. The compounds to be studied will be those for which we have background measurements, but which still require additional information on valence for a more complete understanding.

Progress made during the two-year course of the contract included:

(1) Design and development of a novel monitored beam x-ray absorption spectrometer arrangement to solve the intensity stabilization problem.

(2) Observation of covalency effects in the spectrum of several copper compounds.

(3) Investigation of valence changes associated with conductance and magnetic anomalies in LaCoO_3 .

(4) A study of the sensitivity of absorption edge position to valence in a series of iron compounds.

(5) Investigation of the tetravalent oxidation state of iron.

(6) Investigation of "white-line" spectra in some cyanides and study of relative intensity fluctuations with bonding "p" character.

In the following sections results given in Technical Report No. 1 will be abstracted and later results will be presented in detail.

Conclusions based on these results will then be discussed.

1. Monitored Beam Spectrometer^(1,2)

A diagram of the monitored beam arrangement is presented in Fig. 1. The essential feature is the simultaneous measurement of incident and transmitted beam intensity by passing the incident beam first through a double side-window proportional counter and then through the sample to the detector counter.

2. Spectra of Copper Compounds⁽¹⁾

Divalent copper spectra (Fig. 2) in the compounds $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, CuO , and Cu^{II} oxinate (8-hydroxyquinoline derivative) showed great

similarity in their general features to about 50 ev from the edge regardless of crystal structure or size of the ligands. Significantly, a systematic broadening of the first two peaks is observed when the spectra are classed according to electronegativity of the ligands.

3. Cobalt Spectra in LaCoO_3 ⁽¹⁾

Our interest is in investigating the valence state of cobalt in LaCoO_3 as a function of temperature. Electrical conduction and magnetic susceptibility data suggest that the normally trivalent cobalt in this compound undergoes a sudden disproportionation reaction at about 200°C causing a drastic increase or "anomaly" in both the conductance and susceptibility. Comparison spectra were first obtained for well-defined divalent and trivalent states using CoF_2 and CoF_3 . The trivalent cobalt spectra showed broadened initial peaks by comparison with the divalent case (Fig. 3). This result may be considered consistent with the observed broadening of copper peaks as the bond type becomes more covalent. In general, higher valence states require overlap for stability. In fact, trivalent cobalt compounds generally are stabilized by coordination so that considerable covalent character is often associated with these bonds. These bonds between trivalent cobalt and fluoride could be considered to have a higher degree of overlap than the corresponding bonds with the divalent cobalt.

Spectra of LaCoO_3 obtained at temperatures above and below the conductance transitions showed definite sharpening of the peaks at the elevated temperatures (Fig. 4). Thus spectral evidence consistent with

the formation of a lower valent specie, Co^{2+} is observed. Also, no evidence for a Co^{4+} state was found. This result is to be associated with a valence change rather than a simple temperature effect since generally a broadening of peaks is found on increasing the temperature, while we observed a sharpening of peaks at elevated temperatures.

These results require a reinterpretation of the proposed mechanism of a disproportionation reaction. An alternative to the formation of a Co^{4+} state to account for reduction of Co^{3+} to Co^{2+} could be the formation of O^{1-} . Thus at the conduction anomaly the reaction $\text{Co}^{3+} + \text{O}^{2-} \rightarrow \text{Co}^{2+} + \text{O}^{1-}$ could occur. In order to test this mechanism, measurement of oxygen K-emission spectra of LaCoO_3 would be required.

4. Tetravalent Iron in SrFeO_3

Evidence for a rare tetravalent state of iron has recently been given on the basis of Mössbauer experiments in the perovskite structure SrFeO_3 .^(3,4) X-ray absorption spectroscopy offers an alternative means of examining valence states and hence it seemed useful to obtain x-ray K-absorption spectra of this compound to allow a comparison of results between the two techniques.

Edge Shifts. It has been known for some time that fine structure at the K x-ray absorption edge is sensitive to the valence state of the absorber.⁽⁵⁾ In the case of an ionic solid absorber, details of the spectra for the first 50 ev from the initial steep absorption are not strongly dependent on the crystal symmetry.⁽⁶⁾ The structure of the edge may be analyzed on the basis of optical terms for the isolated next higher

number element. In the first transition series elements the first peak in the edge structure is attributed to a $1s \rightarrow 4p$ transition and is followed by $1s \rightarrow 5p$ transitions with convergent $1s \rightarrow np$ unresolved transitions before the K electron is fully ionized. Such an analysis of the edge structure of argon gas has been done successfully.⁽⁷⁾

At energies higher than about 50 eV from the $1s \rightarrow 4p$ peak extending to 200 eV, additional fine structure is observed and is attributed to scattering of the photoelectron by the lattice and hence this region of the spectrum is sensitive to the crystal structure.⁽⁸⁾

As the oxidation state of a given absorber increases, the edge shifts to higher energy.⁽⁹⁾

The edge shift may be considered as a measure of decreased outer shielding of the nuclear charge as the oxidation state of the absorber is increased. Similar shifts with valence are observed in optical spectral terms.⁽¹⁰⁾ Watson's Hartree-Fock calculations for isolated iron ions in different ionization states show that the $1s$ levels remain relatively constant while the outer levels are shifted to higher energy with increased ionization.⁽¹¹⁾ Edge shifts therefore can be considered to reflect variations in the energy of the outer orbitals with changes in valence.

Mössbauer Studies of SrFeO_3 . The Mössbauer isomer shift obtained for SrFeO_3 ^(12,13) was much smaller than expected for Fe^{IV} based on a simple isolated ion model. This was attributed to considerable covalency in the bonding. Isomer shifts for Fe^{VI} also were found to be less than predicted.⁽¹⁴⁾ Increased covalency in higher oxidation states is expected and is consistent with the broadening of x-ray absorption spectra observed in the case of trivalent cobalt with respect to the divalent ion.

Table I
HFSCF Energies⁽¹¹⁾ (Rydbergs)

		Fe ⁰	Fe ¹⁺	Fe ²⁺	Fe ³⁺
(1s)	=	-675.7103	-675.7103	-675.7100	-675.7094
(2s)	=	-165.3840	-165.3819	-165.3782	-165.3781
(3s)	=	-63.25324	-63.30455	-63.61446	-64.01641
(2p)	=	-164.0475	-164.0456	-164.0416	-164.0429
(3p)	=	-59.51367	-59.63822	-59.93252	-60.43305
(3d)	=	-44.42264	-47.69708	-50.27814	-52.60767
Total Energy	=	-2524.3137	-2524.2856	-2523.3041	-2521.2214

X-Ray Spectra. In the x-ray spectral study of Fe^{IV} we have examined edge shifts with valence to compare SrFeO₃ with divalent and trivalent iron compounds.

Sample spectra are shown in Figs. 5 to 13. Table II presents the results of measurements of peak and edge energies and Fig. 14 gives a plot of these results.

The spectra shown here were normalized to give a relative absorption coefficient based on unit absorption at 200 ev above the edge. At the 200 ev point the amplitude of the extended fine structure has diminished so that the measurement of absorbance, $A = \ln \frac{I_0}{I}$ is not very sensitive to wavelength. The relative absorption coefficients were thus calculated from the relation

$$\mu = \frac{A(\text{ev}) - A(-20 \text{ ev})}{A(200 \text{ ev}) - A(-20 \text{ ev})} .$$

The energy scale is referred to the K edge for iron metal, 7.11120 kev.

The spectra of $\text{SrFeO}_{2.5}$ and SrFeO_3 both show some splitting of the first peak and also considerable broadening by comparison with the ionic fluoride spectra. Broadening of the SrFeO_3 spectrum with respect to the $\text{SrFeO}_{2.5}$ would be expected due to the presence of the high oxidation state for iron. The results may indicate significant covalent iron-oxygen interaction in both compounds. A difficulty arises, however, in the case of $\text{SrFeO}_{2.5}$ which contains both octahedral and tetrahedral coordinated iron in the rhombohedral Brownmillerite structure.⁽⁴⁾

The peak position measurements show shifts to higher energies with increasing oxidation number for the compounds chosen. No significant differences were found between SrFeO_3 and the other Fe^{III} compounds. Difficulty, however, was met in defining a peak position for both $\text{SrFeO}_{2.5}$ and SrFeO_3 due to some splitting of the peak. In both cases the measurements refer to a peak centroid.

Accordingly, measurements of the edge position at half height were made for the compounds since these appear to be more readily defined. It was found that shifts to higher energy with increasing oxidation was again observed.

The data for the oxides and fluorides are displaced to lower energy which reflects the effect of broadening of the line due to the increased covalent interaction in the iron-oxygen bonds relative to the iron-fluoride bonds. A displacement of the edge position of SrFeO_3

Table II

IRON SPECTRA-PEAK AND EDGE ENERGIES

(Energies measured in kev relative to K edge of Fe metal 7.1112 kev)

	<u>Peak</u>	<u>Edge</u>		<u>Peak</u>	<u>Edge</u>
FeF ₂	17.9	12.2	FeF ₃	24.3	18.3
FeO	17.9	9.0	Fe ₂ O ₃	22.4	14.5
FeC ₂ O ₄	17.3				
Fe (ClO ₄) ₂ aq. (1.5 Molar)	17.3		Fe (ClO ₄) ₃ aq. (1.5 Molar)	24.3	
			SrFeO _{2.5}	24.4	14.1
			Fe ₃ O ₄		12.7
			SrFeO ₃	25.0	17.8

to higher energy than that of $\text{SrFeO}_{2.5}$ is observed. The displacement is consistent with assignment of a higher oxidation state than III to iron in SrFeO_3 .

5. Mixed Valence States

An examination of mixed valence states is important at this point since Fe^{IV} could be a mixed Fe^{VI} and Fe^{II} state. Additivity of spectra in the case of mixed cobalt oxides has been previously reported.⁽¹⁵⁾

The spectra of Fe_3O_4 was measured (Fig. 15) since this oxide contains Fe^{II} and Fe^{III} in the spinel structure and could be considered as a mixed spectra of $\text{FeO} + \text{Fe}_2\text{O}_3$. Our spectra of FeO and Fe_2O_3 were summed and renormalized (Fig. 16) for comparison with the experimental Fe_3O_4 spectrum. Our results show that additivity gives a good approximation in this case. The edge position for the Fe_3O_4 spectrum is also close to the 8/3 state in the oxide curve in Fig. 14.

The spectrum of Fe^{VI} in SrFeO_4 was measured (Fig. 17) and found to show a low energy peak such as that observed in KMnO_4 (Fig. 18) which is isomorphous with SrFeO_4 . The sharp peak is apparently characteristic of the strong metal oxygen interactions; Fe^{VI} and Mn^{VII} would be expected only in highly covalent bonding. It appears that no evidence is found for Fe^{VI} in the SrFeO_3 spectrum since no characteristic low energy peak was observed.

6. Highly Covalent Compounds -- The "White Line"

Spectra of the strongly covalent cyanide complexes $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, and $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$ (Figs. 19-21) show an exceptionally sharp,

well-defined line at a wavelength corresponding to the leading edge of the spectra of more ionic iron compounds. Such a line observed previously in the edge of $K MnO_4$ has been termed the "white line" due to its appearance on a photographic plate. Interpretation of the line has not been settled.

A close comparison of this "white line" type of spectra with our ionic spectra gives us a basis for interpretation. We believe that the sharp white line is due to a $1s \rightarrow 3d$ transition which is symmetry forbidden in the absence of a ligand field. The closeness in energy of $4p$ and $3d$ levels causes the white line normally to be unresolved. Resolution of the white line in the nitroprusside spectrum is brought about by the unavailability of $4p$ levels in this compound due to participation of all the $4p$ orbitals in the bonding of this highly covalent structure. Thus absence of $1s \rightarrow 4p$ transitions allows us to see the $1s \rightarrow 3d$ line which is normally unresolved. Absorption at higher energies is due to the $1s \rightarrow 5p$ transition and transitions to higher levels.

7. Intensity and Ionic Character

A relation was searched for between the intensity of the first peak, the $1s \rightarrow 4p$ transition, and the availability of $4p$ orbitals. The intensity of the first peak would be expected to vary inversely with p -character in the bonding, since involvement of $4p$ orbitals in bonding should decrease the $1s \rightarrow 4p$ transition probability in the first transition series.

Spectra of the series of manganese compounds MnO , MnS , and $MnSe$ were measured to note the variation of first peak intensity with decreasing

ionic character. The spectra are shown in Figs. 22-24 and Table III presents the ionic character of the bonding, estimated from electronegativity differences⁽¹⁶⁾ and the relative intensities of the first peak.

Table III

First Peak Intensity Dependence on Ionic Character

	<u>Ionic Character</u>	<u>$\mu-1$ (1st peak)</u>
MnO	0.63	0.61
MnS	0.22	0.25
MnSe	0.19	0.25
MnTe	0.09	--

The results indicate that correlation of intensity with μ character in bonding may be an important additional use of x-ray absorption spectroscopy. Agreement of the relative estimates in the table is embarrassingly close and merely fortuitous.

Discussion

In this study x-ray absorption spectroscopy has been applied to the solution of definite solid state chemistry problems in valence determinations and variation of intensity and ionic character has been observe.

Postulated cobalt valence changes with temperature in LaCoO_3 based on interpretation of magnetic and electrical conduction data were confirmed. Also, Mössbauer studies of iron in SrFeO_3 which indicated that iron is in a higher oxidation state than III were corroborated.

The study of "tetravalent" iron in SrFeO_3 emphasized the practical possibility of using sensitivity of absorption edge wavelength in valence investigations. Demonstration of additivity of spectra in comparing the spectra of Fe_3O_4 with the composite spectra of FeO and Fe_2O_3 showed that the presence of an ion in several valence states may be determined and also that caution must be used in assigning a valence on the basis of wavelength positions alone. For example, a net "tetravalent" iron valence state could possibly be the composite of a Fe^{II} and an Fe^{VI} . The spectra of SrFeO_4 showed that Fe^{VI} has a characteristic "white-line" shape and thus could be distinguished in a mixed valence state.

Observed spectral intensity changes with variation in bonding were used in investigating cobalt valence changes in LaCoO_3 rather than edge shifts. Systematic relative intensity variations with variation in bond type were observed in the study. Correlation of intensities with ionic character or "p" orbital density was made in the case of the extreme white-line spectra of cyanide complexes and a systematic trend in relative intensities with ionic character was found in halogen and chalcogen series. These results show that relative intensity determinations can be used in investigating bond type or ionic character.

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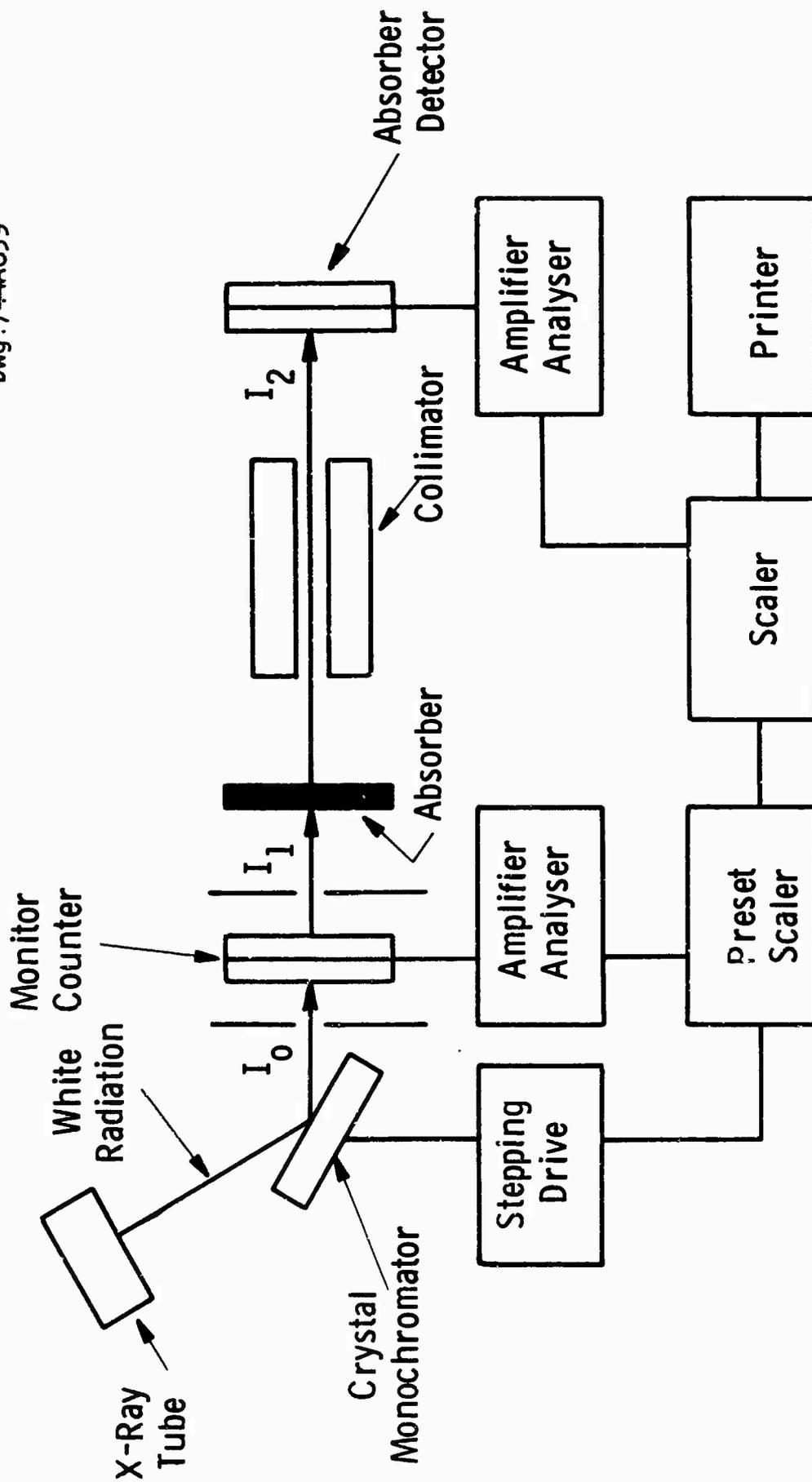


Fig. 1—Monitored beam x-ray spectrometer

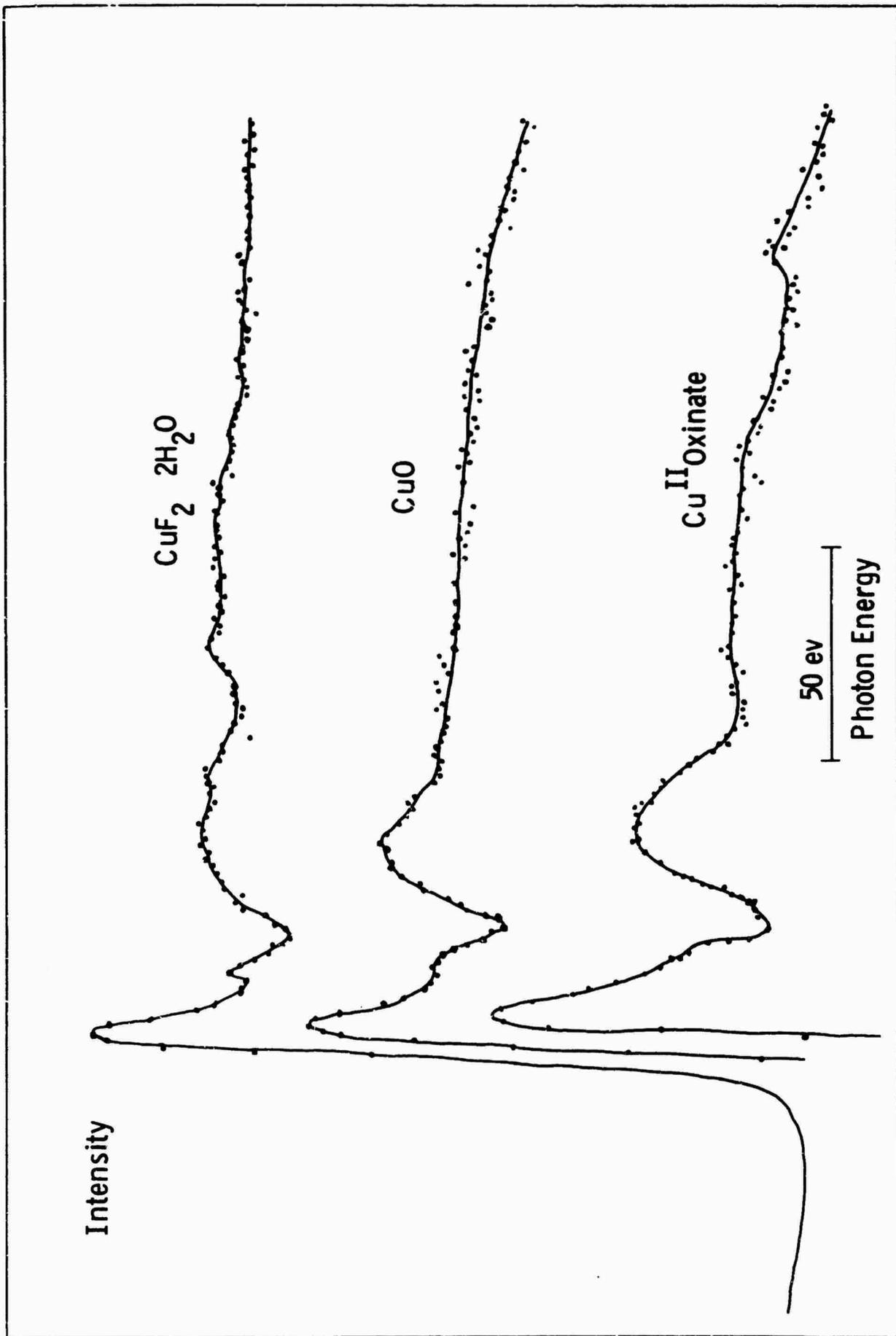
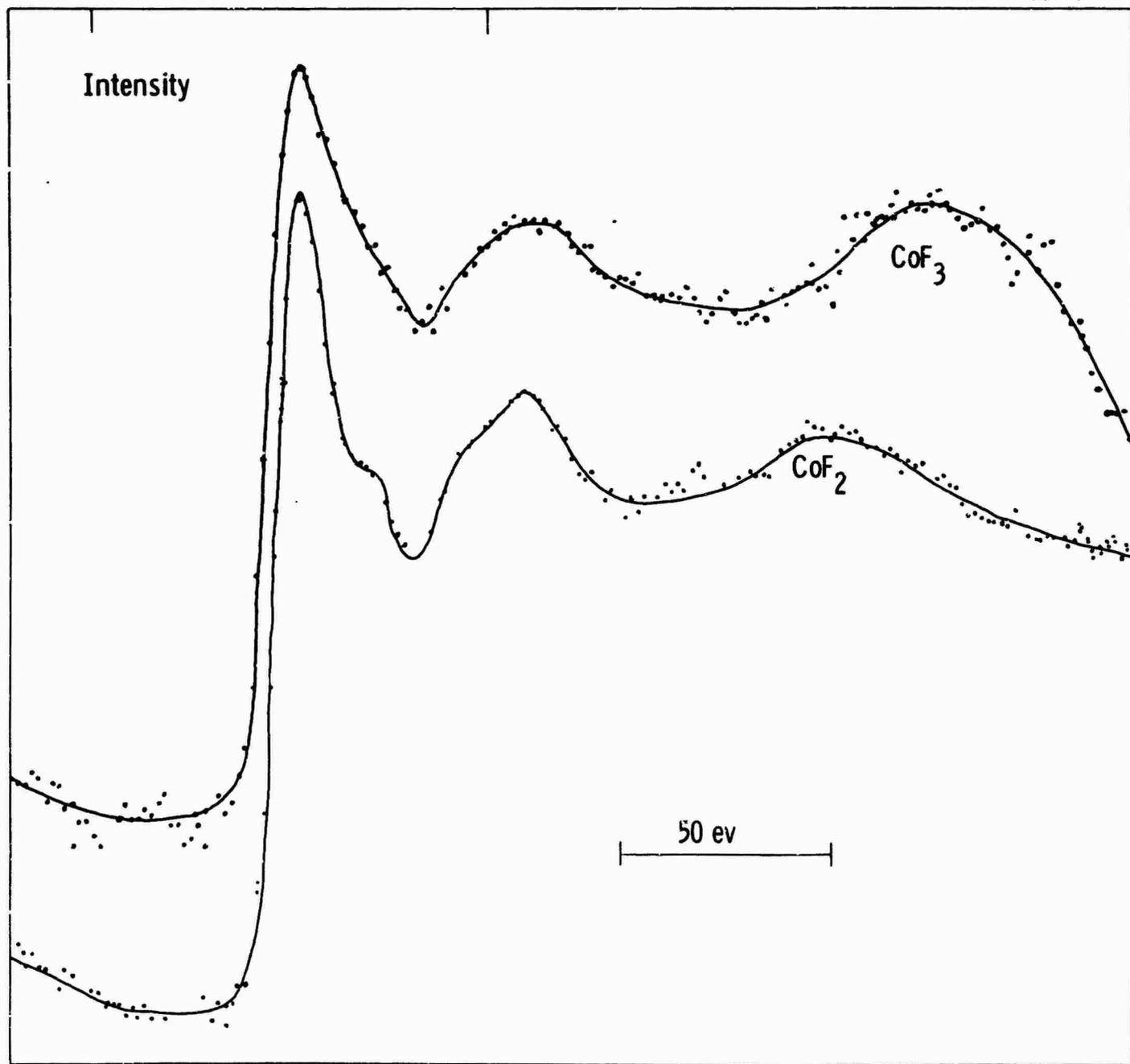


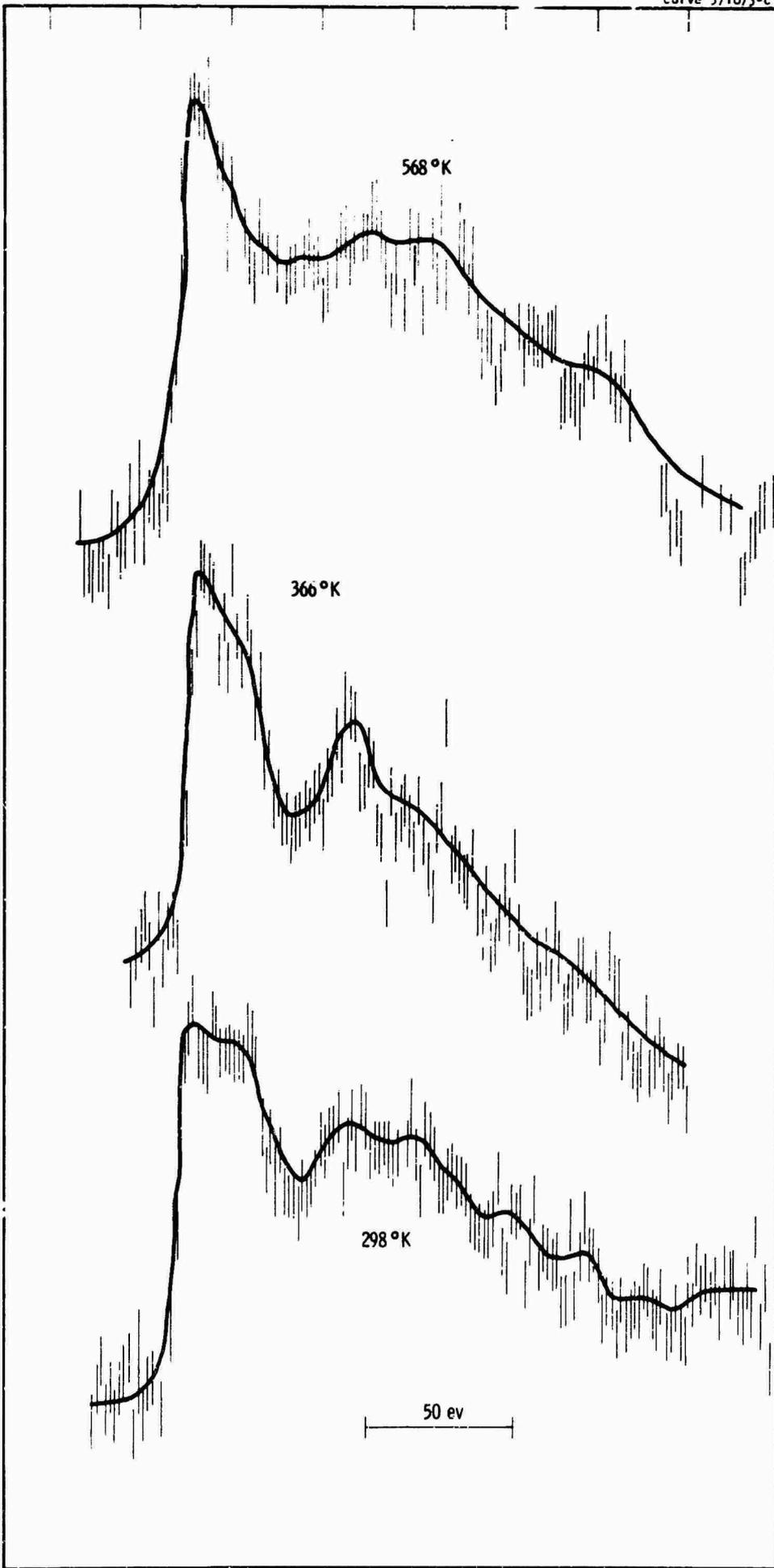
Fig. 2— Divalent copper spectra



Photon Energy

Fig. 3— Cobalt spectra

Intensity



Photon Energy

Fig. 4- Cobalt spectra in LaCoO₃.

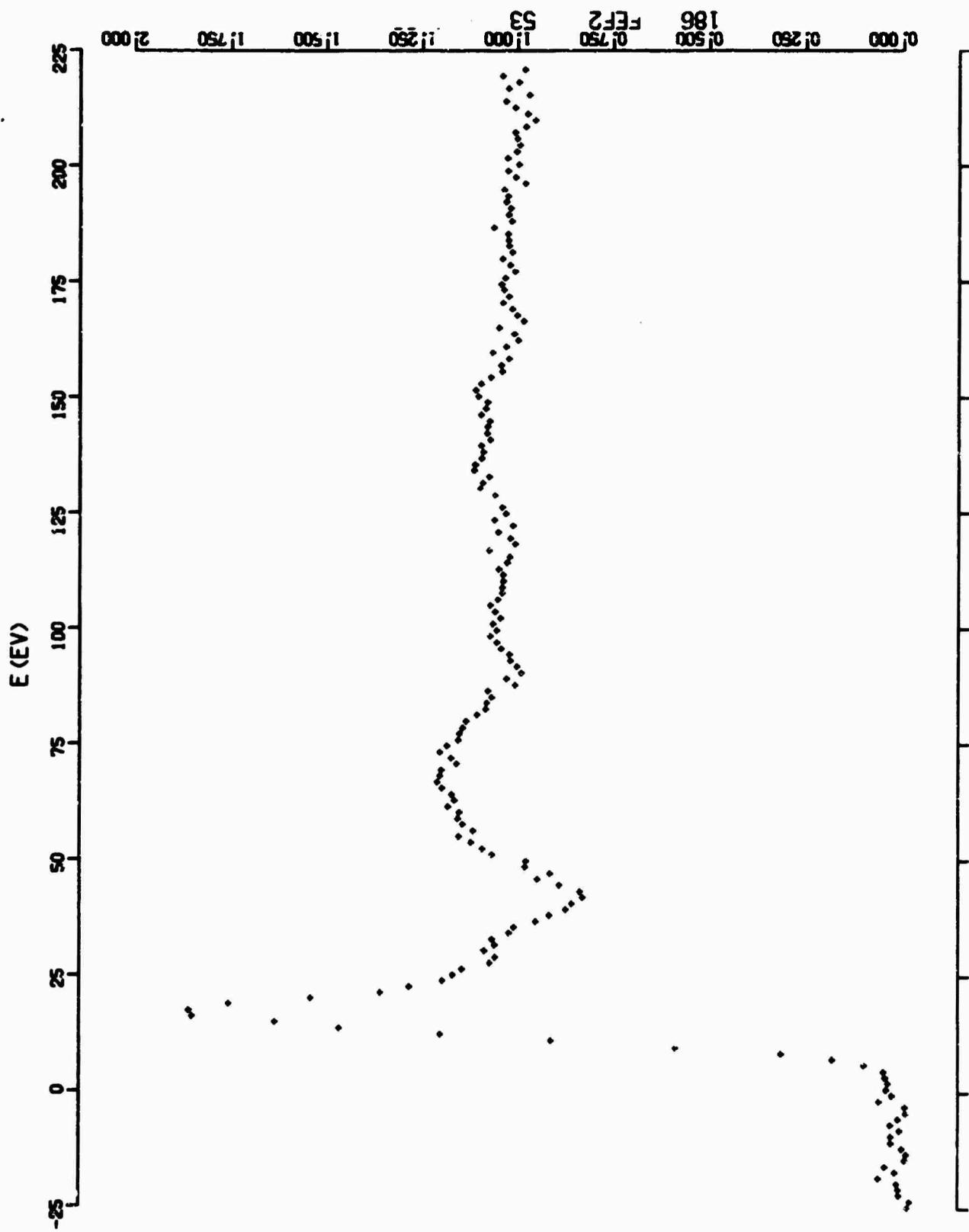


Fig. 5-FeF₂

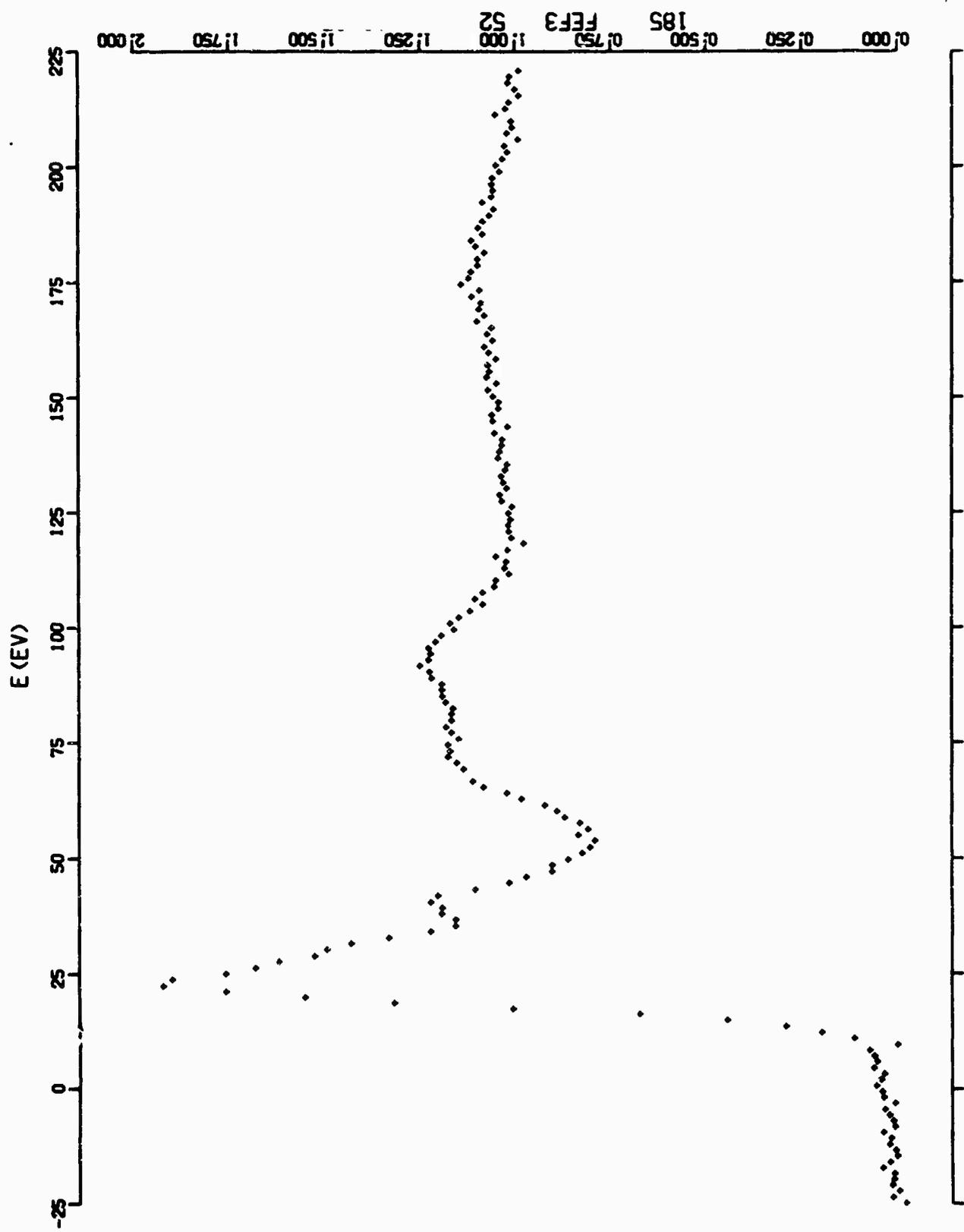


Fig. 6- FeF₃

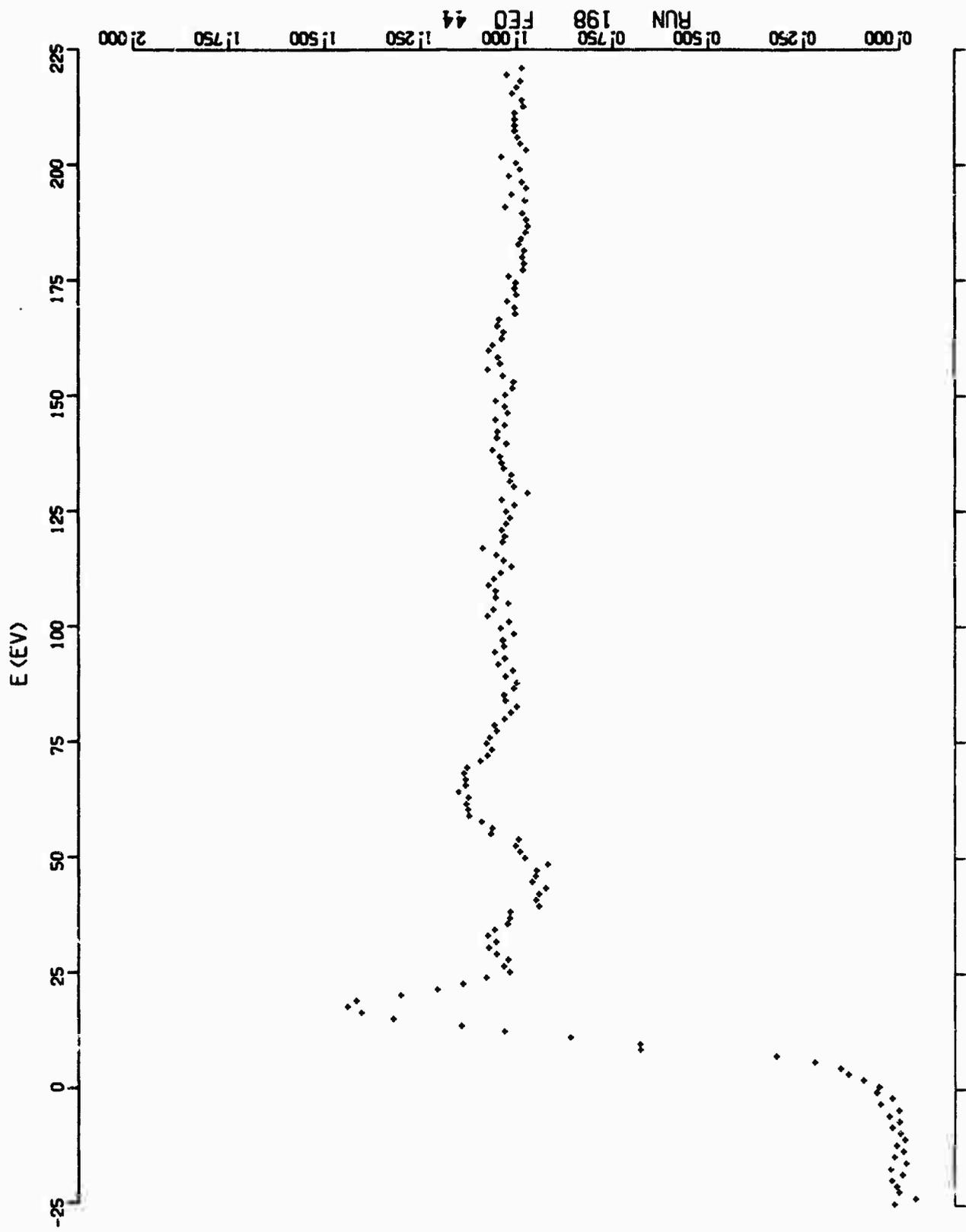


Fig. 7 - FeO

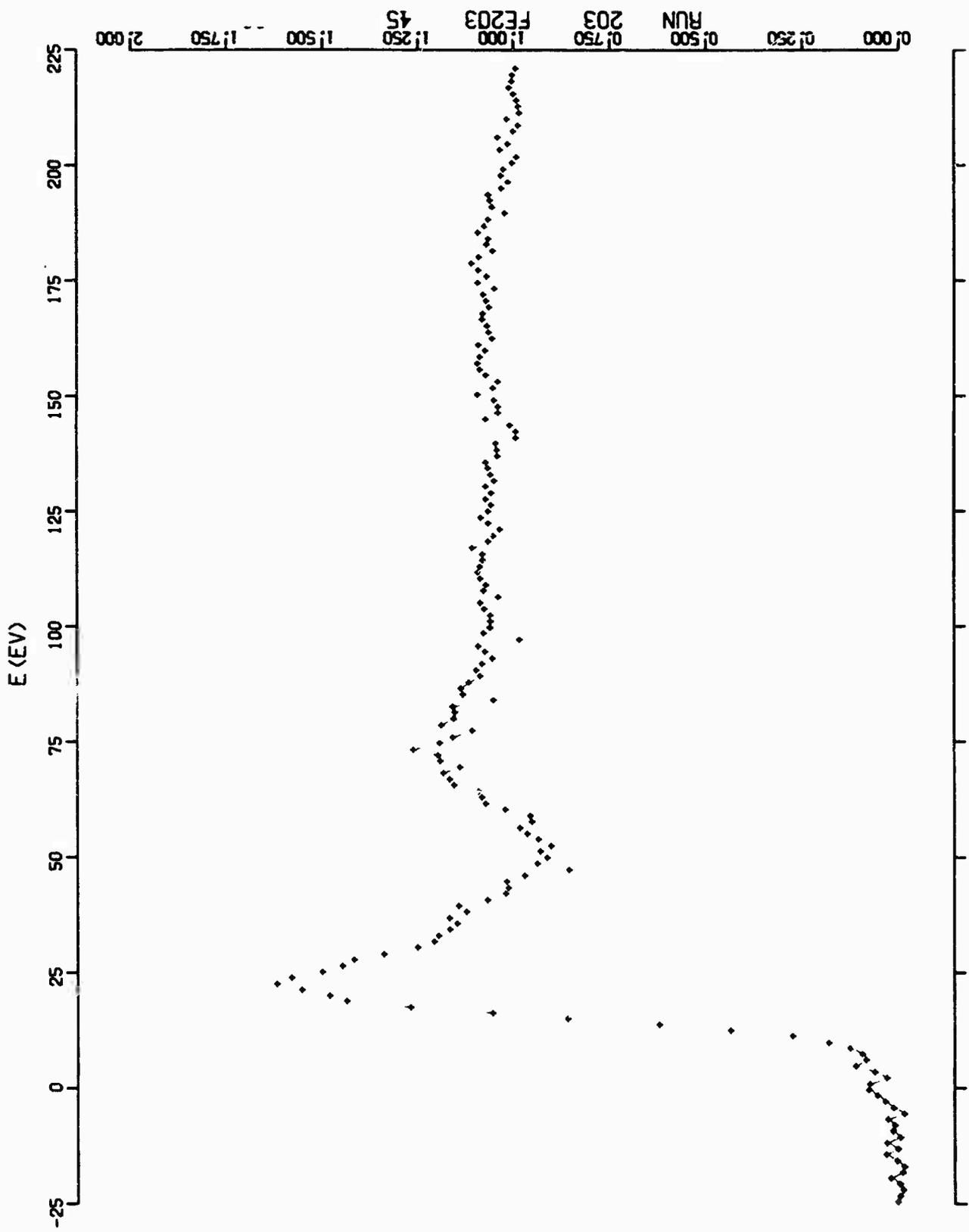


Fig. 8— Fe_2O_3

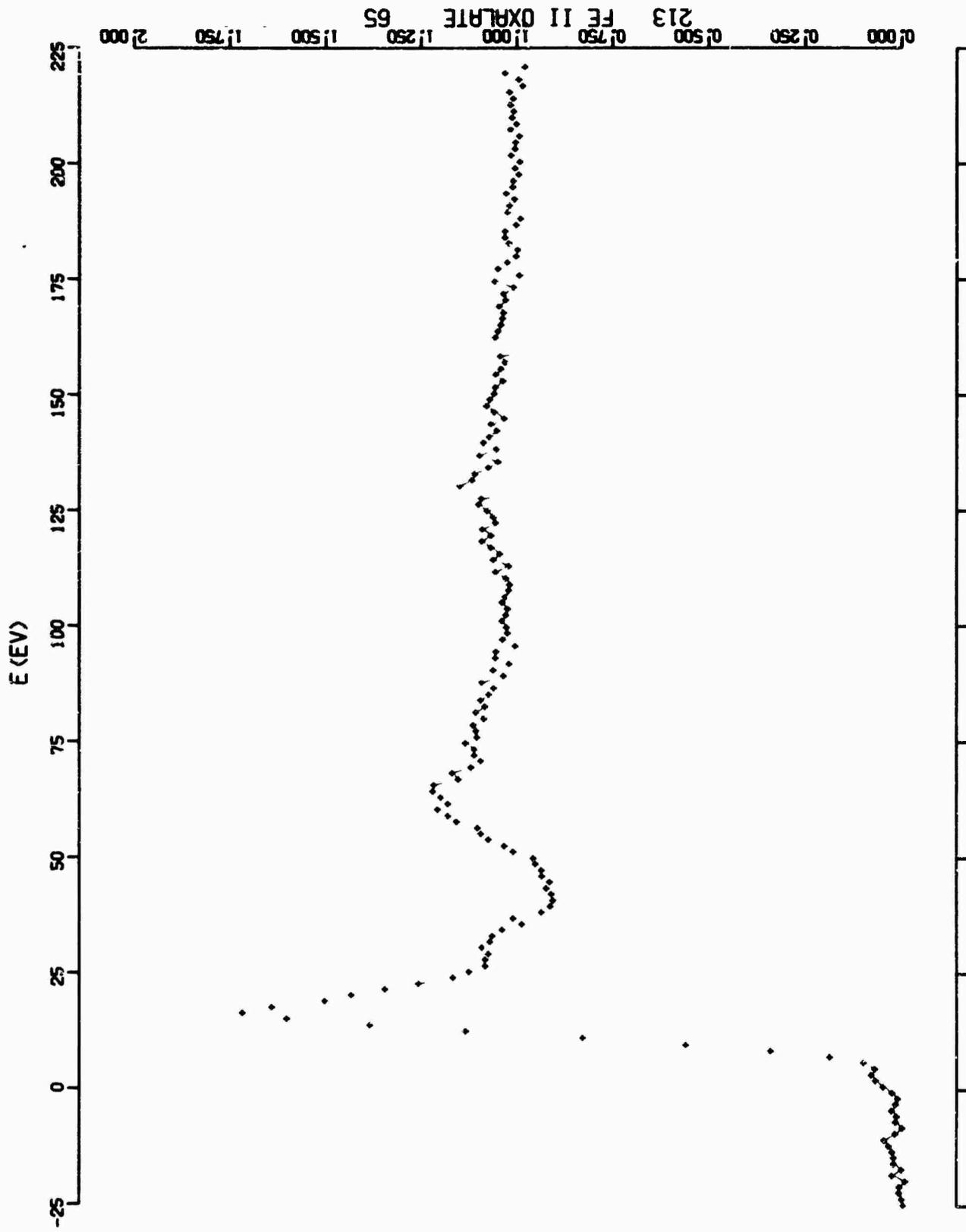


Fig. 9—FeC₂O₄

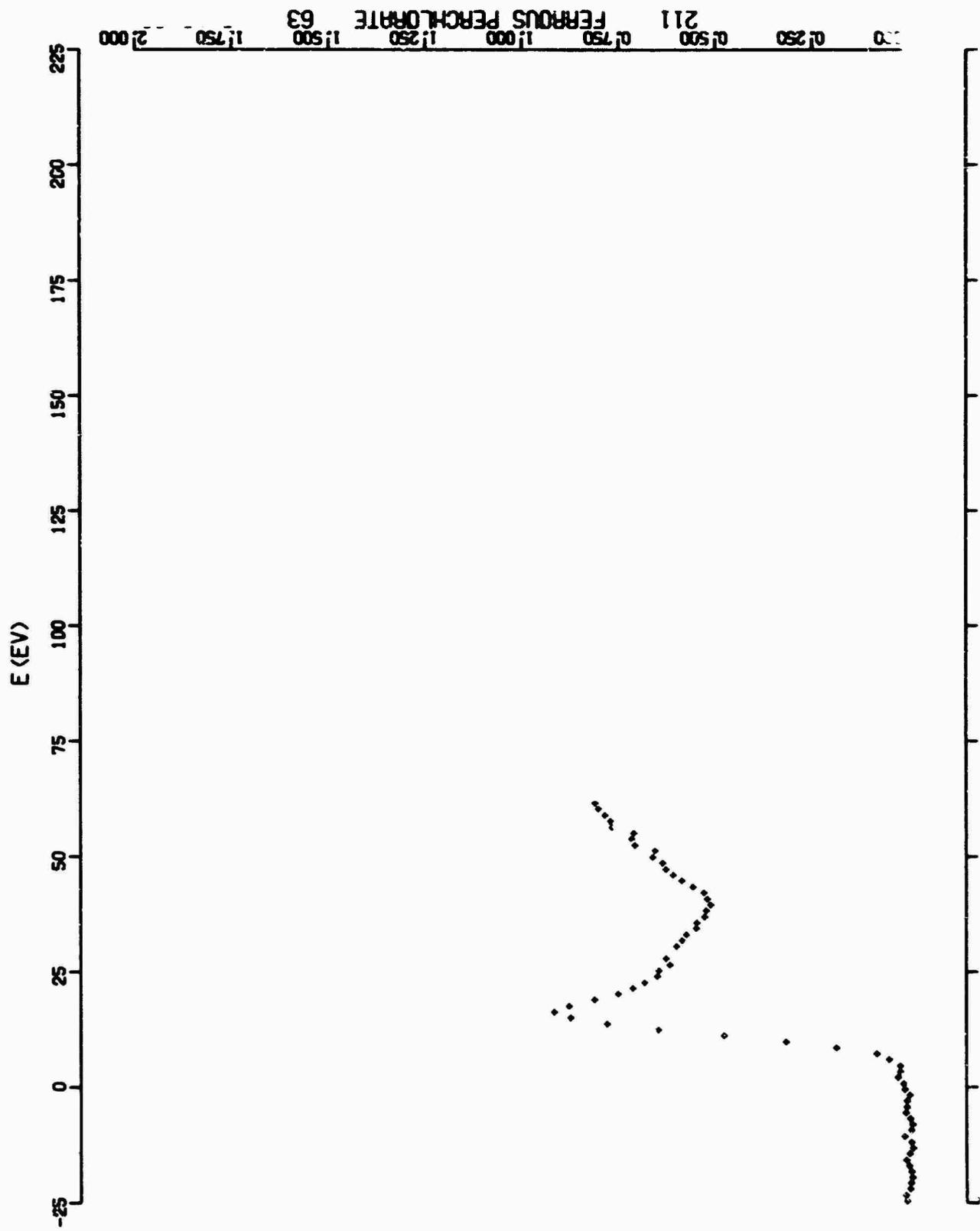


Fig. 10— $\text{Fe}(\text{ClO}_4)_2$ aq. 1.5 molar

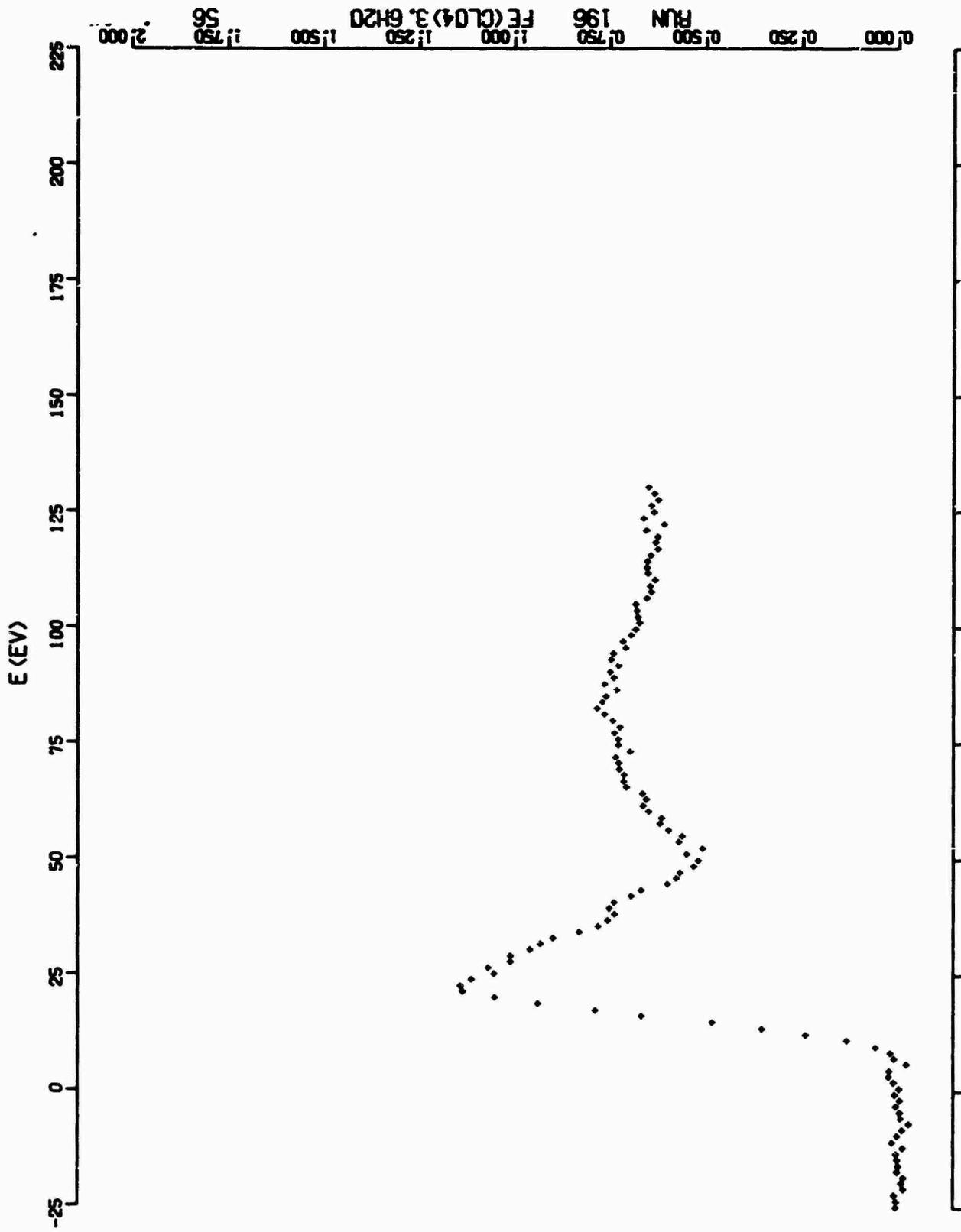


Fig. 11—Fe(ClO₄)₃ aq. 1.5 molar

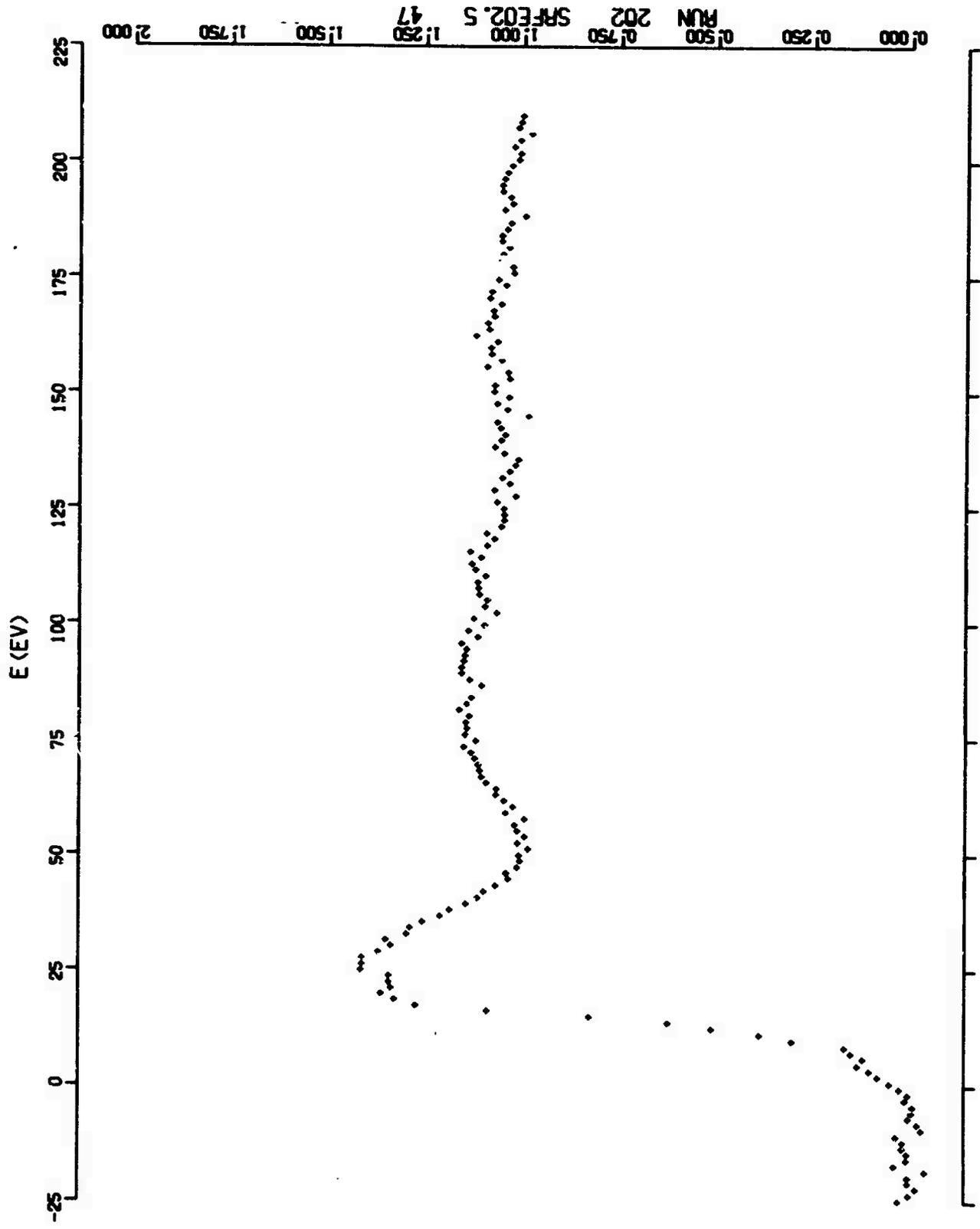


Fig. 12-- SrFeO_{2.5}

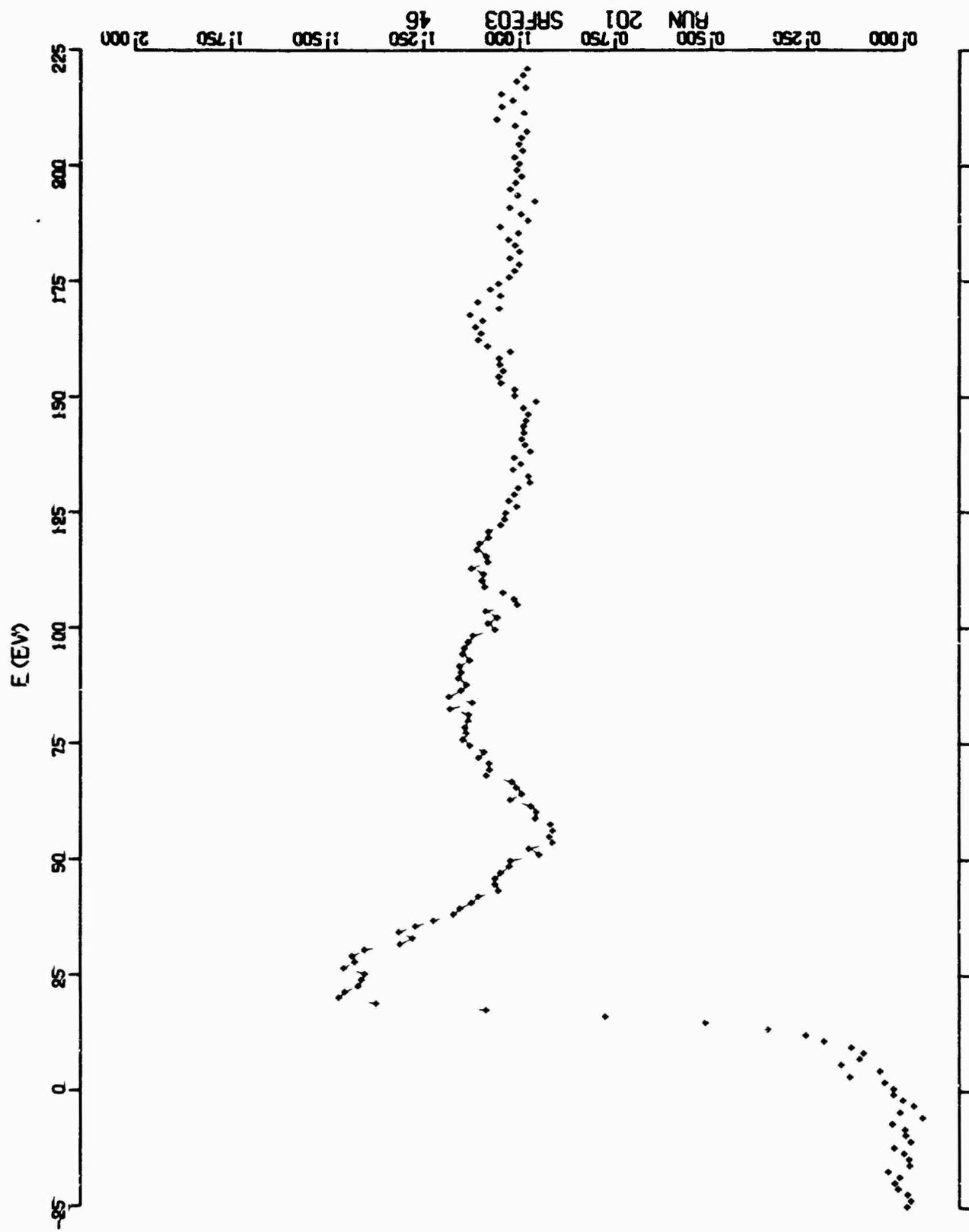


Fig. 13-- SrFeO₃

Curve 577992-A

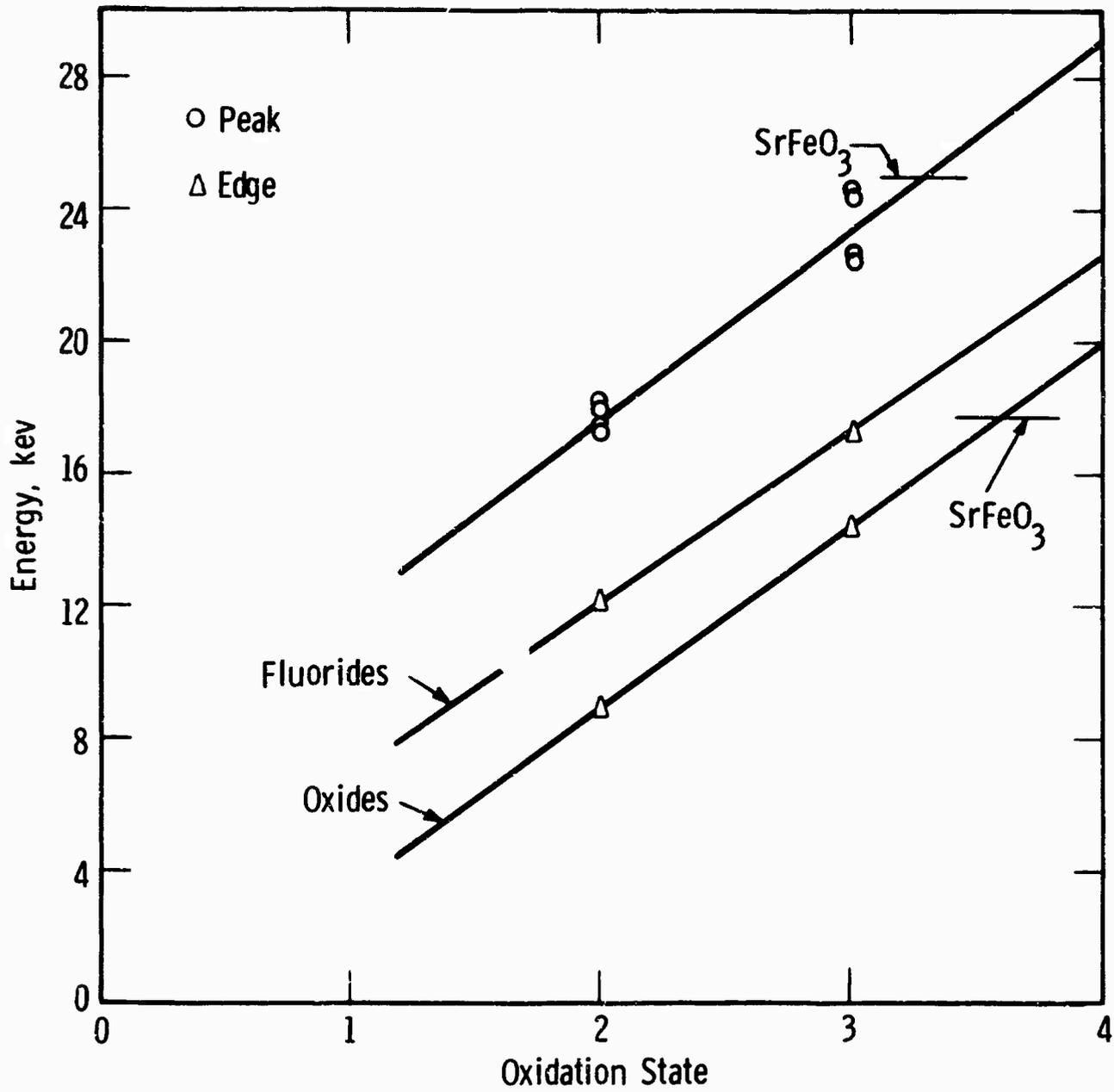


Fig. 14 - Iron spectra-peak and edge energies

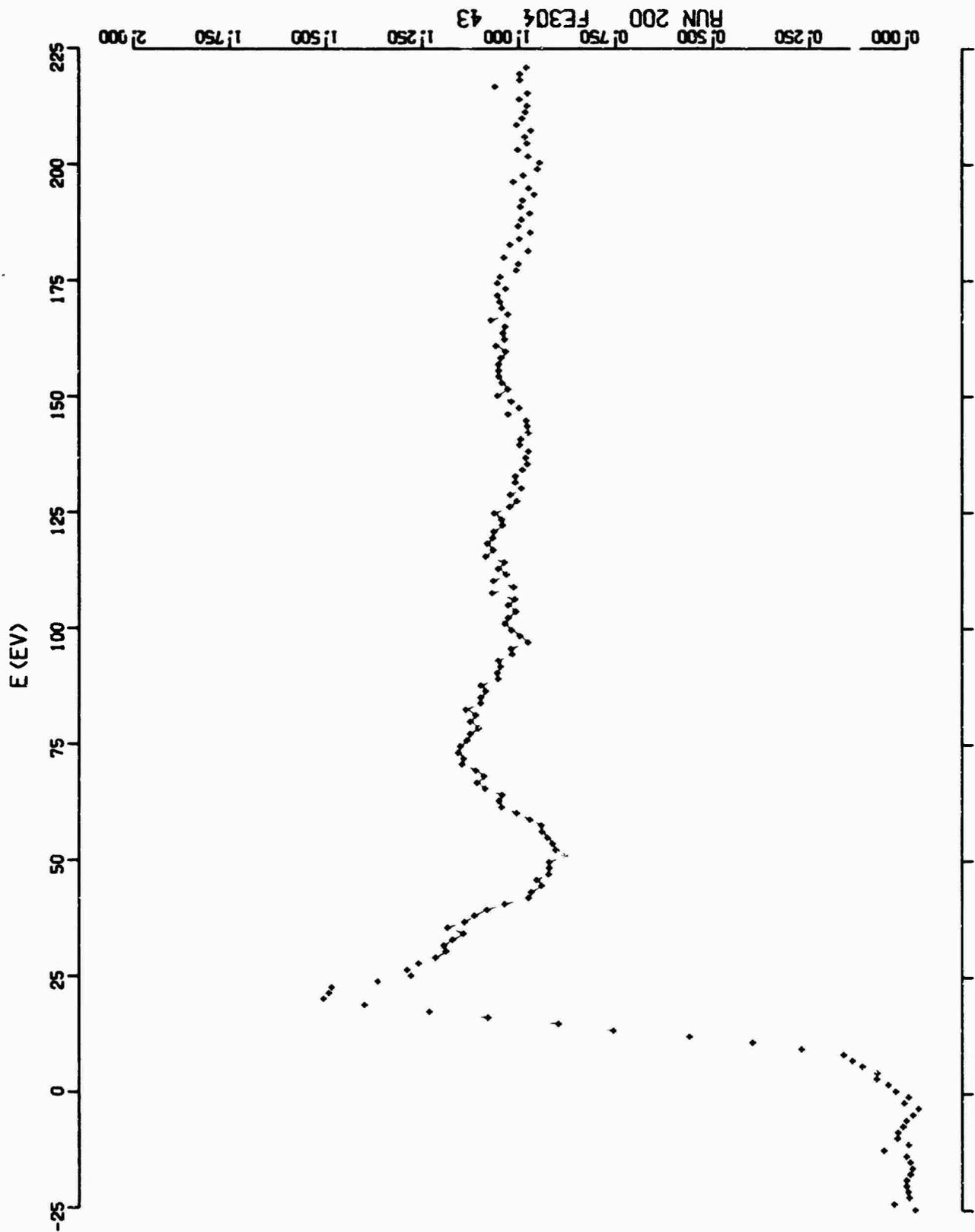


Fig. 15—Fe₃O₄

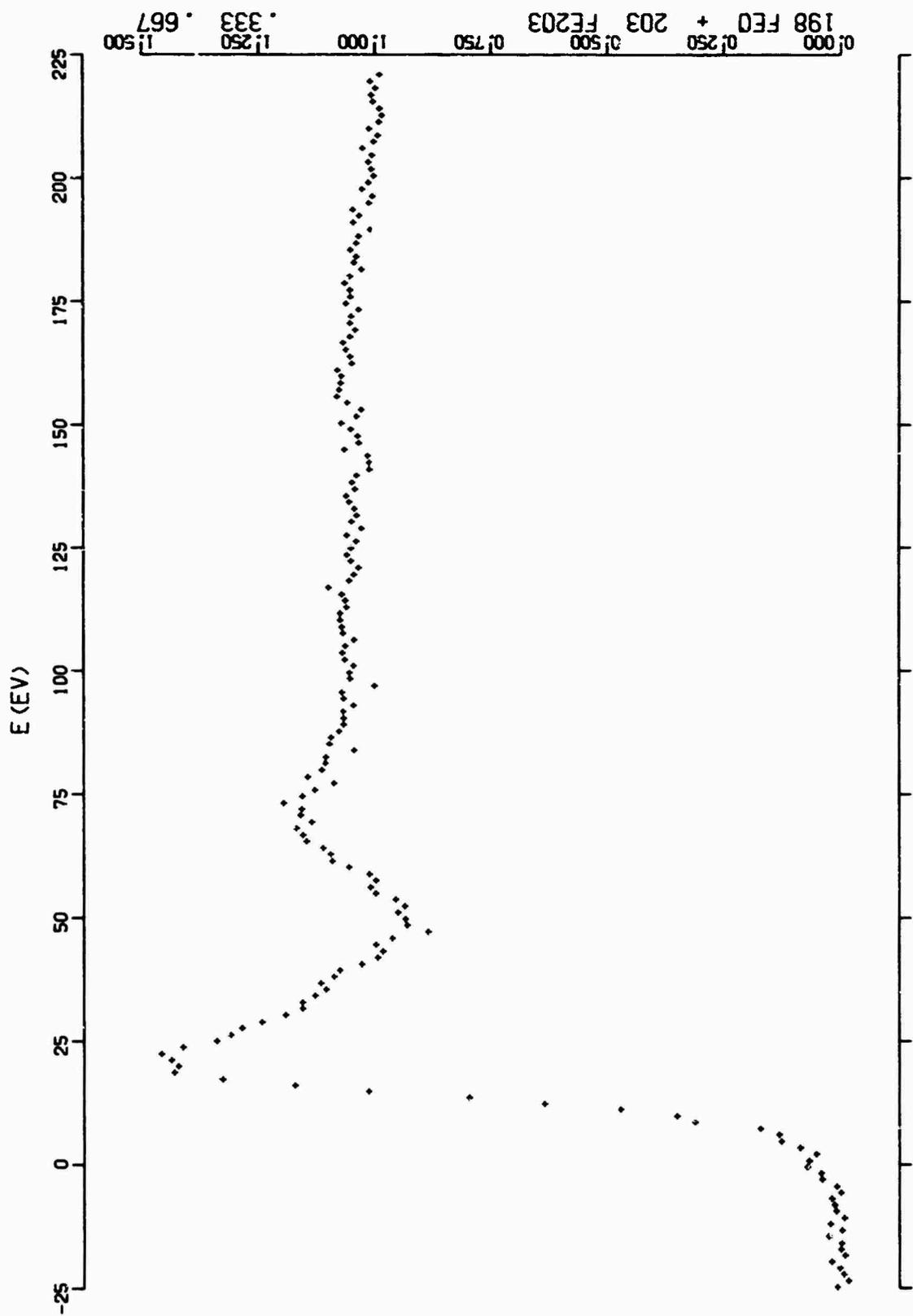


Fig. 16-FeO + Fe₂O₃

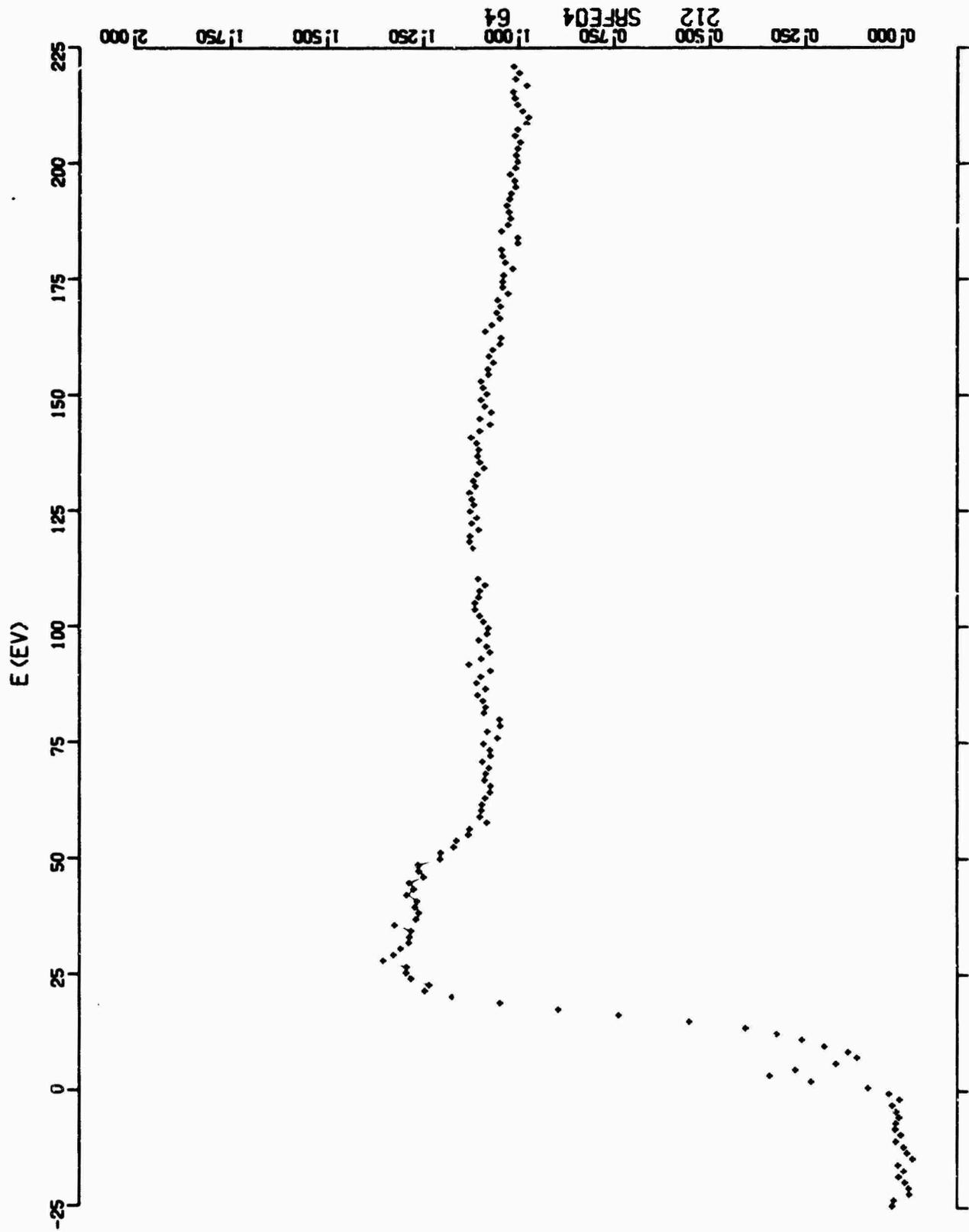


Fig. 17—SrFeO₄

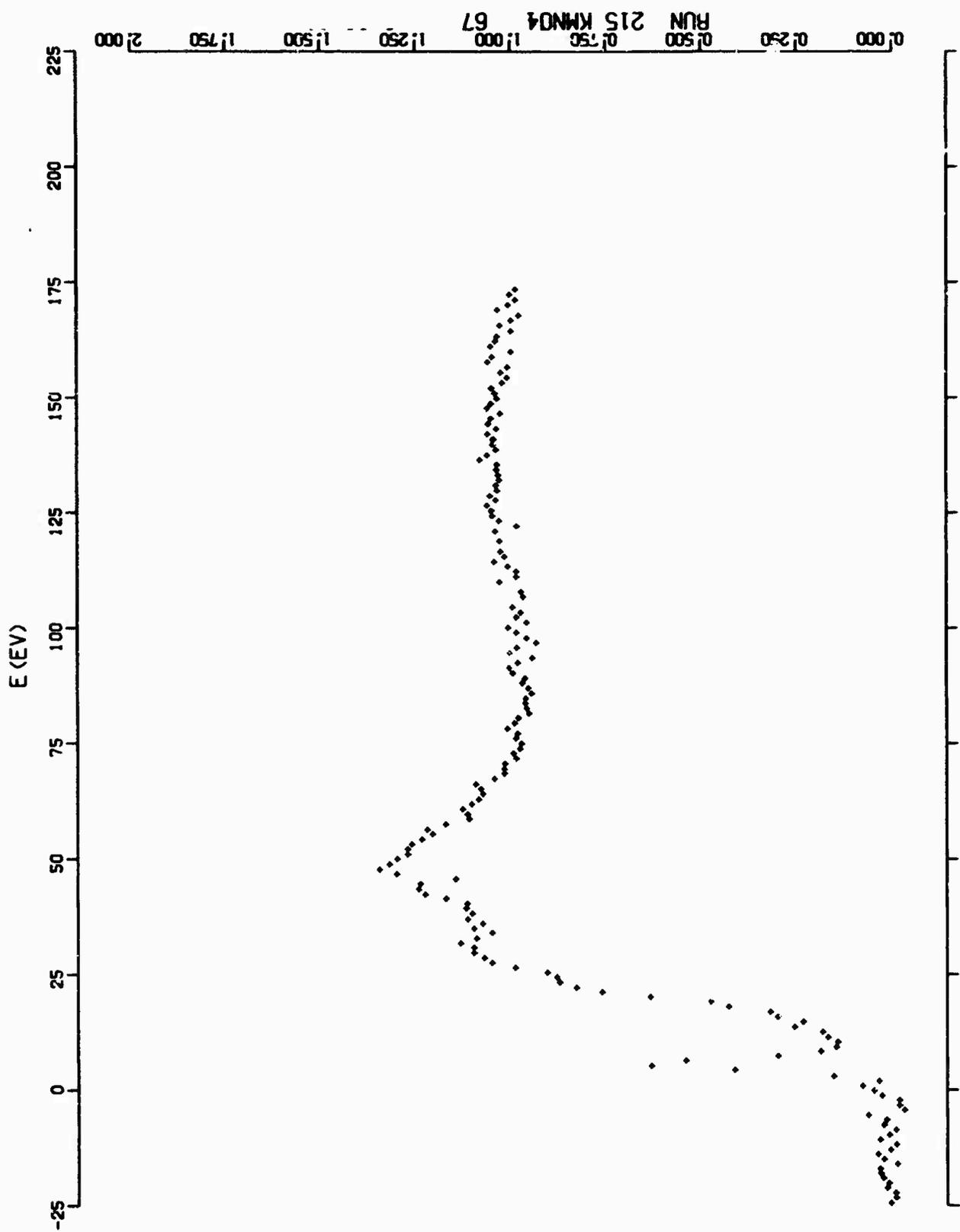


Fig. 18— KMnO_4

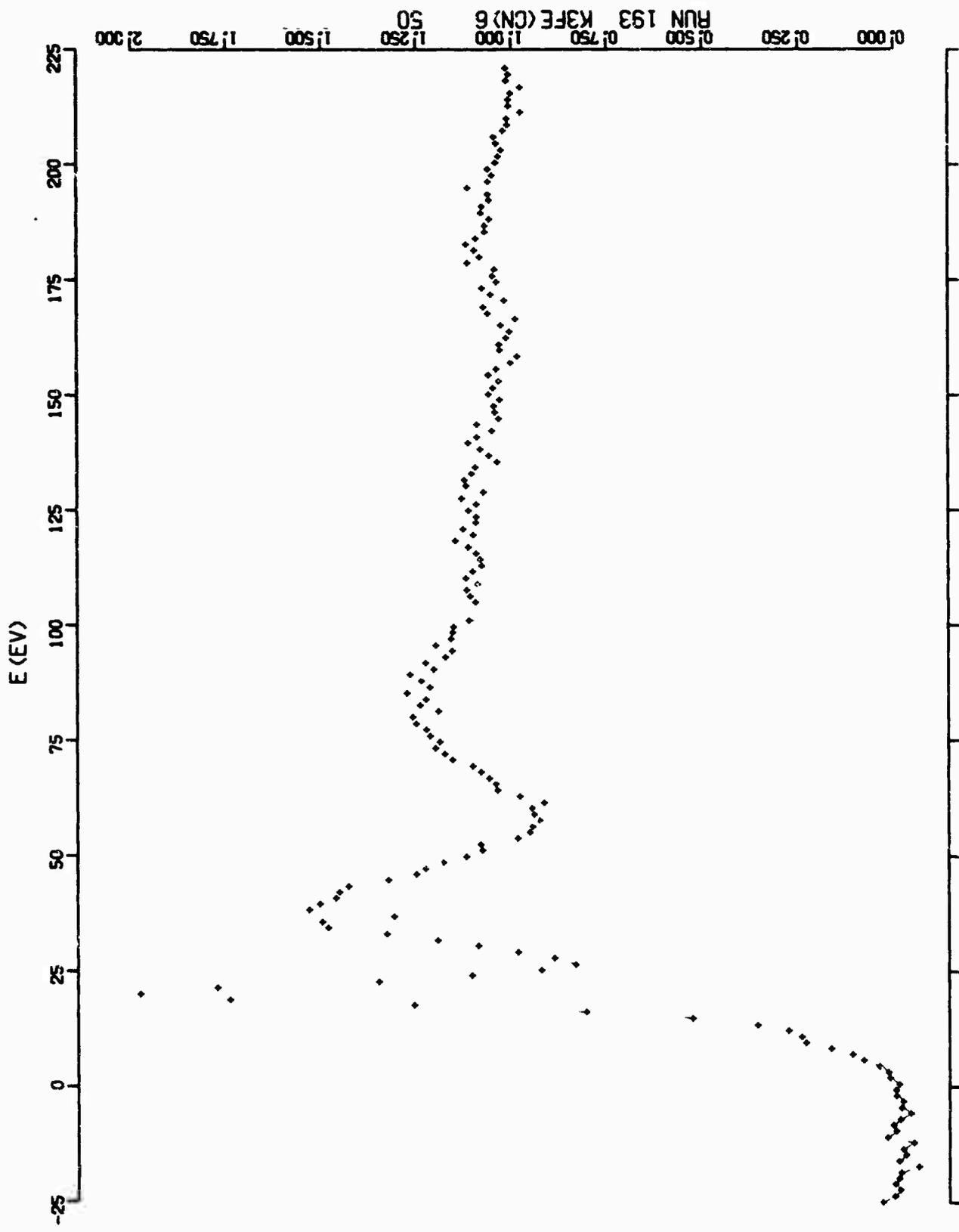


Fig. 19— $K_3Fe(CN)_6$

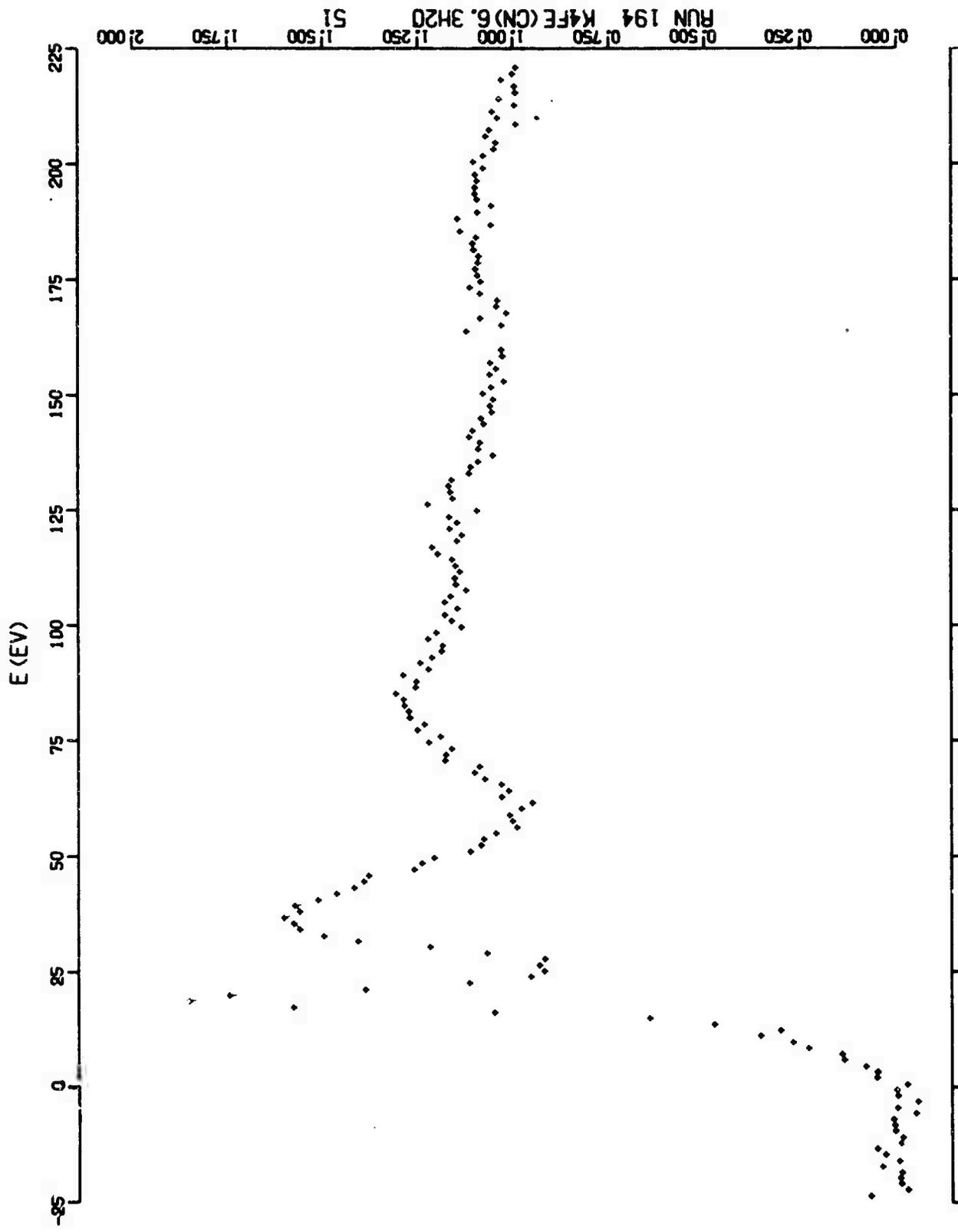


Fig. 20— $K_4Fe(CN)_6 \cdot 3H_2O$

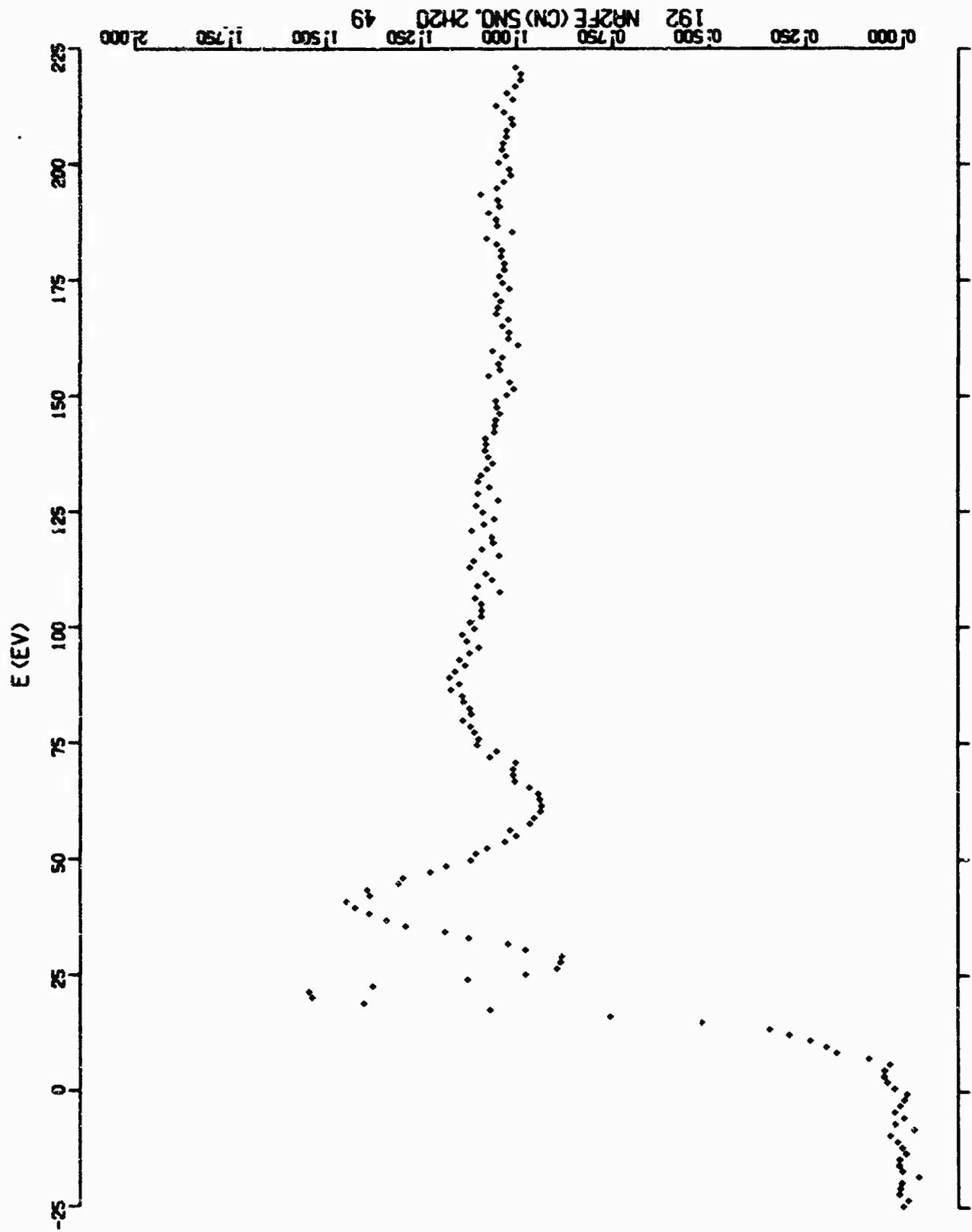


Fig. 21 - $\text{Na}_2(\text{CN})_5 \cdot \text{NO} \cdot 2\text{H}_2\text{O}$

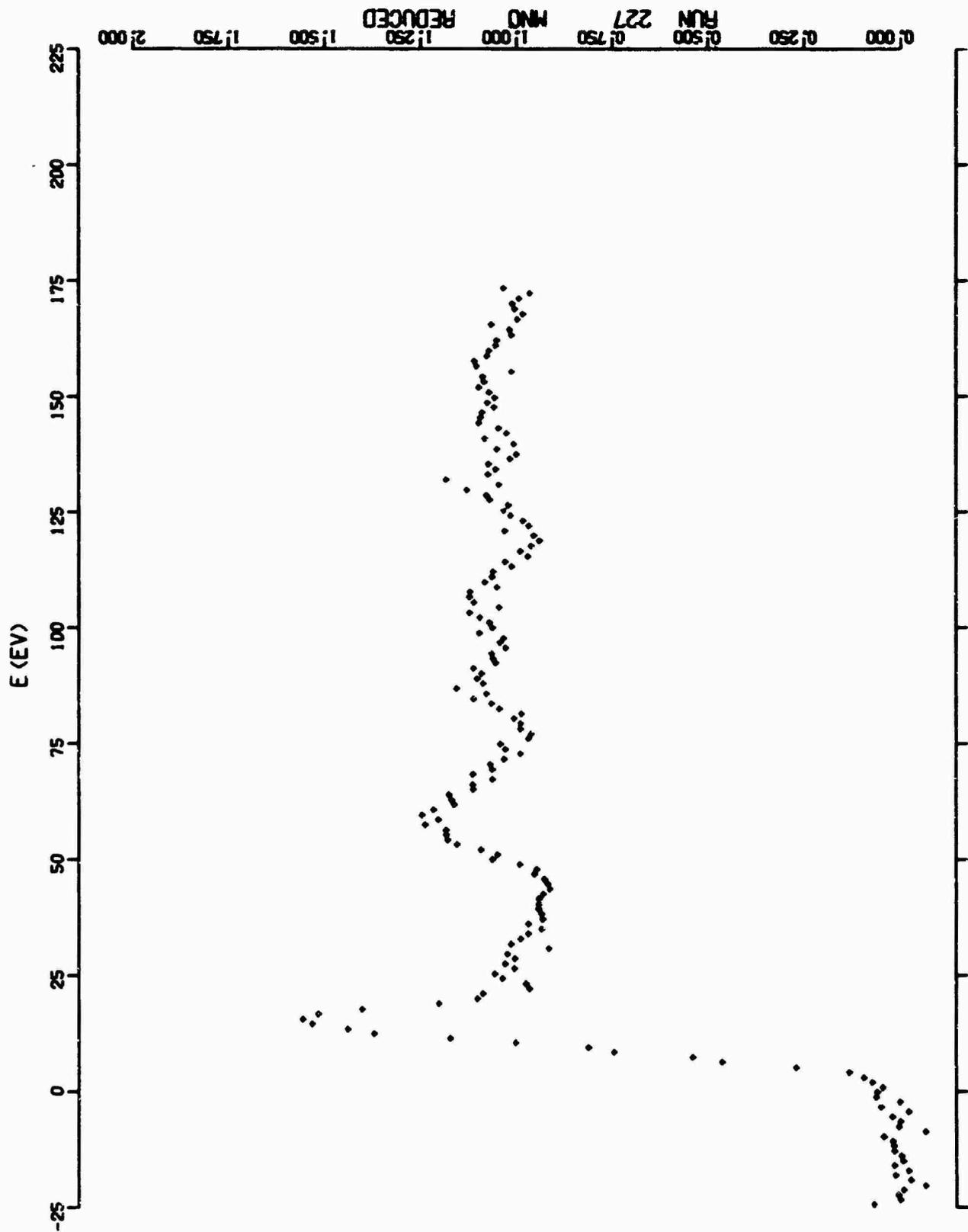


Fig. 22—MnO

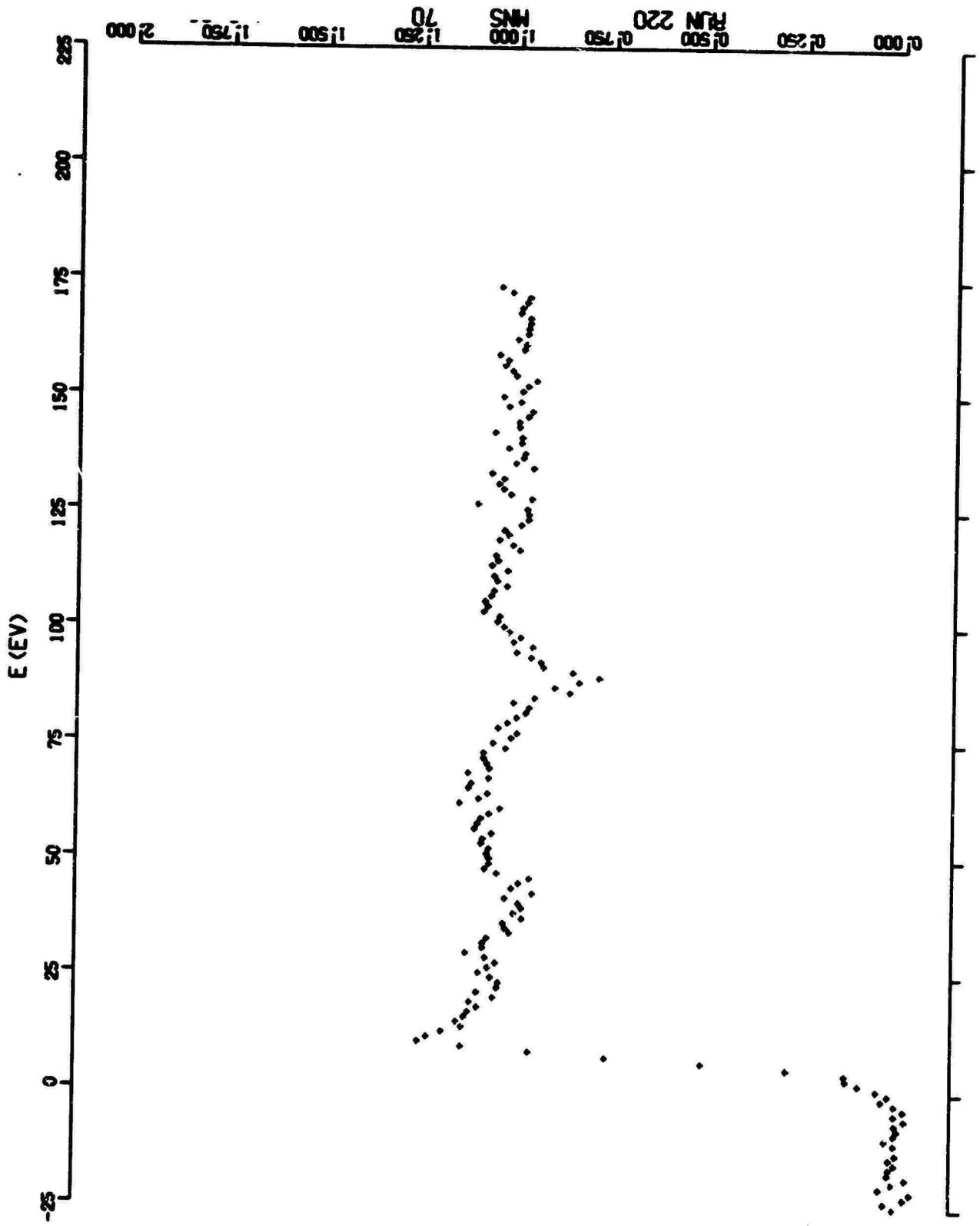


Fig. 23—Mn S

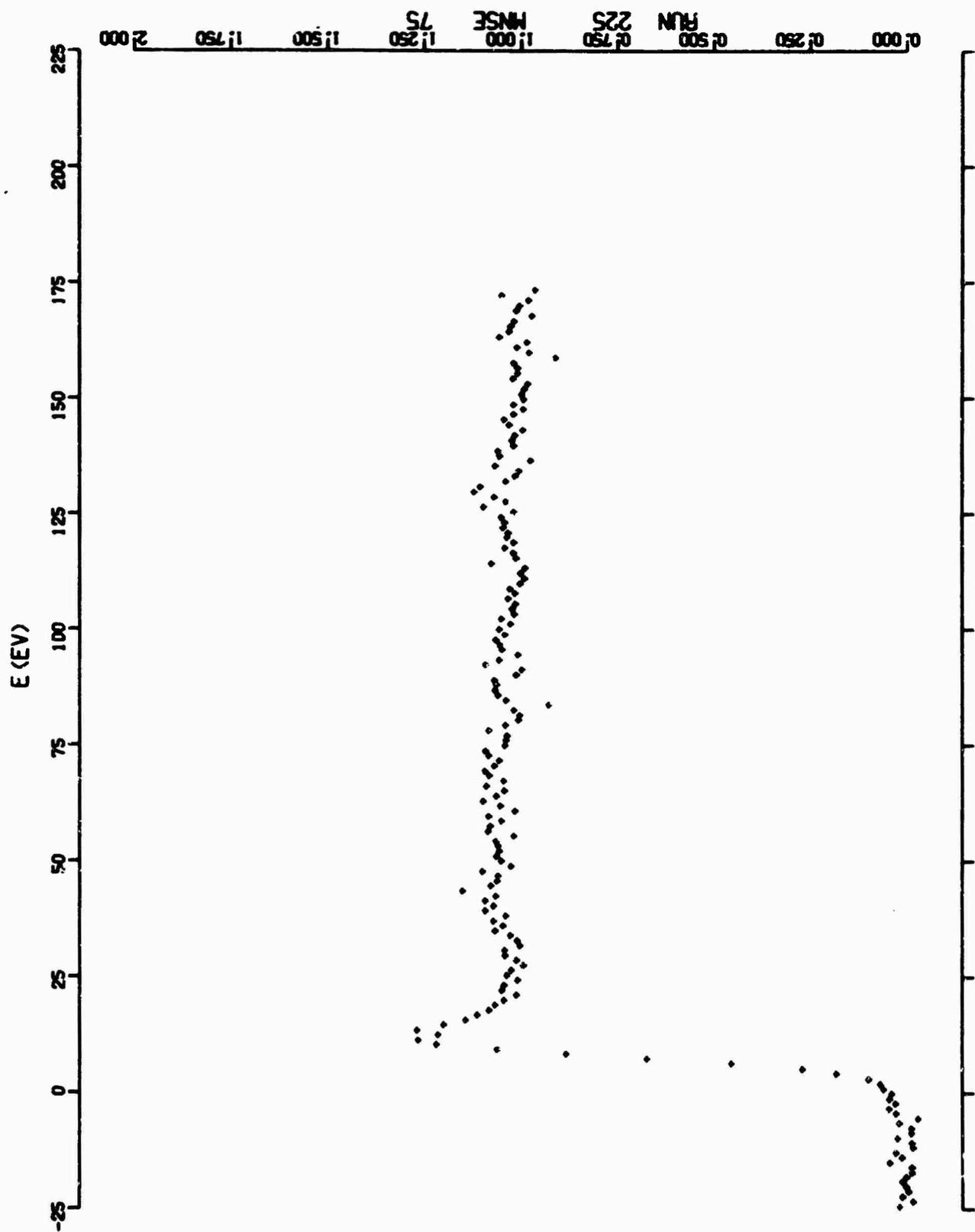


Fig. 24—MnSe