

AD734761

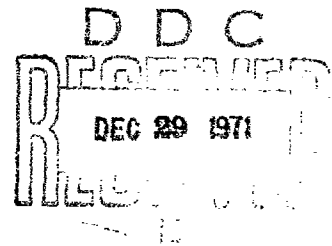
AFML-TR-71-165

**INFRARED DISPERSION ANALYSIS AND OPTICAL  
CONSTANT SPECTRA OF  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (HEMATITE)**

*CONRAD M. PHILLIPPI  
STEPHEN R. LYON*

TECHNICAL REPORT AFML-TR-71-165

JUNE 1971



Approved for public release; distribution unlimited

Reproduced by  
**NATIONAL TECHNICAL  
INFORMATION SERVICE**  
Springfield, Va. 22151

**AIR FORCE MATERIALS LABORATORY  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

R

41

UNCLASSIFIED  
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE INFRARED DISPERSION ANALYSIS AND OPTICAL CONSTANT SPECTRA OF $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> (HEMATITE)			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
5. AUTHOR(S) (First name, middle initial, last name) Conrad M. Phillippi Stephen R. Lyon			
6. REPORT DATE		7a. TOTAL NO. OF PAGES 32	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-71-165	
b. PROJECT NO. 7360 and 7353		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c. Task No. 736005 and 735302			
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433	
13. ABSTRACT Infrared reflection spectra of the ordinary and extraordinary rays of single crystal ferric oxide ( $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> ) in the form of the mineral hematite are isolated and measured. Dispersion analyses are performed on these spectra and the best-fit resonance parameters are identified, along with estimated tolerances. Longitudinal optical mode frequencies are calculated from these data. Also calculated are: refractive index, extinction coefficient, absorption coefficient, and real and imaginary parts of the dielectric constant of both rays. These are presented as tabulations between 4000 and 200 cm <sup>-1</sup> , and as plots between 700 and 200 cm <sup>-1</sup> . Several oxidation film spectra from pure iron are illustrated and discussed.			

DD FORM 1 NOV 65 1473

UNCLASSIFIED  
Security Classification

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

ADDITION	
CFSTI	WHITE SECTION <input checked="" type="checkbox"/>
DOC	DIFF SECTION <input type="checkbox"/>
MAN. GEN.	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
DIST.	AVAIL. and/or SPECIAL
<del>A</del>	

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

UNCLASSIFIED  
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Hematite Ferric Oxide Reflection Spectrum Dispersion Analysis Oxidation						

UNCLASSIFIED  
Security Classification

**INFRARED DISPERSION ANALYSIS AND OPTICAL  
CONSTANT SPECTRA OF  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (HEMATITE)**

*CONRAD M. PHILLIPPI  
STEPHEN R. LYON*

Approved for public release; distribution unlimited

## ABSTRACT

Infrared reflection spectra of the ordinary and extraordinary rays of single crystal ferric oxide ( $\alpha\text{-Fe}_2\text{O}_3$ ) in the form of the mineral hematite are isolated and measured. Dispersion analyses are performed on these spectra and the best-fit resonance parameters are identified, along with estimated tolerances. Longitudinal optical mode frequencies are calculated from these data. Also calculated are: refractive index, extinction coefficient, absorption coefficient, and real and imaginary parts of the dielectric constant of both rays. These are presented as tabulations between 4000 and 200  $\text{cm}^{-1}$ , and as plots between 700 and 200  $\text{cm}^{-1}$ . Several oxidation film spectra from pure iron are illustrated and discussed.

## FOREWORD


This report was prepared by the Analytical Branch, Materials Physics Division, in collaboration with the Advanced Metallurgical Studies Branch, Metals and Ceramics Division, both of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. This work was conducted under Project 7360, "Chemical, Physical, and Thermodynamic Properties of Aircraft, Missile, and Spacecraft Materials", Task 736005, "Compositional, Atomic, and Molecular Analysis of Experimental Materials for Advanced Air Force Systems", and Project 7353, "Characterization of Solid Phase and Interphase Phenomena in Crystalline Substances", Task 735302, "Correlation of Physical and Mechanical Properties of Metals and Ceramics", by Conrad M. Phillippi (LPA), Research Physicist and Stephen R. Lyon (LLS), Research Metallurgist.

This report covers work performed between June 1970 and March 1971. The manuscript was submitted by the authors in June 1971.

The authors gratefully acknowledge the contributions of David W. Fischer of the Analytical Branch for the generous loan of the hematite crystals from his collection and his continuing interest in this work.

The work described herein is a selected part of a general study into the application of infrared and Raman spectroscopic techniques to the characterization of oxidation and corrosion products and processes of Air Force metals and alloys. Ferric oxide is a prominent oxidation product of ferrous alloys.

This technical report has been reviewed and is approved.

  
FREEMAN F. BENTLEY, Chief  
Analytical Branch  
Materials Physics Division

## TABLE OF CONTENTS

SECTION	PAGE
INTRODUCTION	1
EXPERIMENTAL	3
DISPERSON ANALYSIS	5
OPTICAL CONSTANT SPECTRA	8
APPLICATION EXAMPLE	8
REFERENCES	10



## ILLUSTRATIONS

FIGURE		PAGE
1.	Specular Reflectance Attachment for PE #225 Sample Compartment	17
2.	Optical Geometry for Isolating Ordinary and Extra- ordinary Ray Spectra of Uniaxial Crystals	18
3.	Unpolarized Reflection Spectrum From Pyramidal Face of Hematite	19
4.	Ordinary and Extraordinary Reflection Spectra of Hematite	20
5.	Measured (Solid Line) and Best Fit Calculated (Circles) Ordinary and Extraordinary Reflection Spectra of Hematite	21
6.	Refractive Index Spectrum of Ordinary Ray of Hematite	22
7.	Refractive Index Spectrum of Extraordinary Ray of Hematite	23
8.	Extinction Coefficient Spectrum of Ordinary Ray of Hematite	24
9.	Extinction Coefficient Spectrum of Extraordinary Ray of Hematite	25
10.	Absorption Coefficient Spectrum of Ordinary Ray of Hematite	26
11.	Absorption Coefficient Spectrum of Extraordinary Ray of Hematite	27
12.	Spectrum of the Real Part of the Dielectric Constant of Ordinary Ray of Hematite	28
13.	Spectrum of the Real Part of the Dielectric Constant of Extraordinary Ray of Hematite	29
14.	Spectrum of the Imaginary Part of the Dielectric Con- stant of Ordinary Ray of Hematite	30
15.	Spectrum of the Imaginary Part of the Dielectric Con- stant of Extraordinary Ray of Hematite	31
16.	Reflection Spectra of Oxidation Films on Pure Iron	32

## INTRODUCTION

The oxidation and corrosion products of Air Force metals and alloys are particularly amenable to study by infrared spectroscopic techniques. The realtime characterization of oxidation films growing in situ by means of infrared reflection spectroscopy is being developed by this laboratory (Ref 1). To characterize such a film it is necessary to know 1) its optical constant spectra and 2) the assignment of various spectroscopic features to specific vibrational species of its crystal lattice. Optical constant data are used in equations to quantitatively describe the physical properties of films (thickness, orientation, homogeneity) from spectroscopic measurements. Vibrational assignments are necessary for identifying the various oxides in multi-component films and for resolving anomalies which appear in the oxidation spectra of new alloy systems. This is especially important where the films are optically anisotropic and may exhibit preferential orientation effects.

In the characterization of oxidation films on ferrous alloys,  $\alpha\text{-Fe}_2\text{O}_3$  is one of the oxides frequently encountered. In the mineral form, this oxide is hematite and it occurs as large single crystals with surfaces suitable for direct measurement of optical properties. With appropriate precautions, a single crystal may be considered to be an infinitely thick oriented oxidation film. The optical constants, therefore, of the bulk single crystal can be used as a first approximation to those of an oxidation film. In this study, natural crystal faces were measured to avoid possible spectral changes due to lattice damage from the optical grinding and polishing required to prepare oriented artificial surfaces.

Several large natural single crystals of hematite from Goyaz, Brazil, were available for measurement. The black metallic-like crystals displayed large

well-developed smooth faces, several of which were perpendicular to, and nearly parallel to, the optic axis. These surfaces observed by reflection in nearly normally incident polarized radiation were sufficient for isolation of the ordinary ( $\omega$ ) and extraordinary ( $e$ ) ray spectra. In effect (Ref 2) these spectra are associated with lattice vibrations perpendicular to and parallel to the optic axis, respectively. The impurities in the crystal used for primary measurements, as determined by emission spectroscopy, are listed in Table I.

$\alpha$ - $\text{Fe}_2\text{O}_3$  belongs to the rhombohedral system and can be referenced to either rhombohedral or hexagonal crystal axes. It is described by the space group  $D_{3d}^6$  with two  $\text{Fe}_2\text{O}_3$  molecules in the rhombohedral unit cell (Ref 3). A factor group analysis for  $\text{Fe}_2\text{O}_3$  predicts the following optical activity (Ref 4):

Infrared active	2 $A_{2u}$ (ENC) 4 $E_u$ (EIC)
Raman active	2 $A_{1g}$ 5 $E_g$
Optically inactive	2 $A_{1u}$ 3 $A_{2g}$

Of importance to these measurements is the expectation of finding two infrared active fundamental modes in the  $e$ -ray (ENC) and four more in the  $\omega$ -ray (EIC). Ferric oxide is isomorphous with the sesquioxides of aluminum, chromium, gallium, rhodium, titanium, and vanadium, and these modes have been isolated and assigned in at least  $\text{Al}_2\text{O}_3$  (Ref 5) and  $\text{Cr}_2\text{O}_3$  (Ref 6).

## EXPERIMENTAL

The double-beam spectrometer employed in these measurements is a PE Model 225 infrared grating spectrophotometer which covers the range 4000 to 200  $\text{cm}^{-1}$ . The sample beam intensity is so great that absorbing samples such as these hematite crystals reach equilibrium temperatures on the order of 80°C. The spectrometer is equipped with a wire grid polarizer located at the entrance slit to the foreprism monochromator and common to both beams. Having an AgBr substrate its useful range of transmission extends only to 280  $\text{cm}^{-1}$ , and so spectra from 280 to 200  $\text{cm}^{-1}$  were measured in unpolarized radiation.

The specular reflectance attachment inserted in the sample beam is shown in Fig. 1. The average angle of incidence is 15°. With no similar attachment in the reference beam there is some unbalance at the atmospheric absorption lines but this is minimized by purging the instrument with dry nitrogen. Furthermore, the 100% line is not flat and this effect is compensated by measuring sample reflectances relative to those of an evaporated gold mirror in the same position. In these particular measurements no correction was made for mirror reflectances being less than unity, because this error tends to compensate for scattering losses from the less-than-perfect crystal faces. The sample is mounted on a 6-degree of freedom goniometer, enabling precise positioning of a surface in the beam. Measurement procedure consisted of 1) mounting a crystal face in the goniometer with the optic axis in a selected orientation relative to the plane of incidence 2) adjusting the orientation of the face for peak reflected signal 3) selecting the plane of polarization relative to the plane of incidence 4) scanning the sample reflection spectrum and repeating with the mirror substituted for the sample 5) reading the two spectra

at intervals of  $5 \text{ cm}^{-1}$  or less depending on steepness, and calculating the reflection coefficient as the ratio.

Fig. 2 illustrates the optical configurations by means of which the ordinary and extraordinary ray spectra may be isolated, assuming faces parallel to and perpendicular to the optic axis are available. Four of these configurations isolate a ray independently of the angle of incidence; they are  $\epsilon = S:S$  and  $\omega = N:S = S:P = P:S$ . To provide an alternate configuration for confirmation of extraordinary ray isolation,  $\epsilon = P:P(0)$  can also be approximated by a  $15^\circ$  angle of incidence ( $P:P(15^\circ)$ ).

A natural face parallel to the optic axis (necessary for the  $P:S$ ,  $S:P$ ,  $S:S$ , and  $P:P(0)$  configurations) and large enough to fill the sample beam for absolute reflectances was not present on these crystals. However, a small face inclined at an angle of only  $10^\circ 8'$  to the optic axis, as determined by optical goniometric measurement, was found which enabled the above configurations to be approximated. Using this face,  $\omega$  and  $\epsilon$ -ray spectra could be isolated but absolute reflectances could not be measured accurately. However, as described below, absolute reflectances were determined from amply large (0006) and (11 $\bar{2}$ 3) faces.

Fig. 3 shows the full unpolarized reflection spectrum from a pyramidal face; this is a mixture of  $\omega$  and  $\epsilon$  spectra. The frequencies of the three minima and one maximum are approximate and are so designated for discussion purposes. The  $500 \text{ cm}^{-1}$  minimum was found between  $500.5$  and  $495 \text{ cm}^{-1}$  off various faces and polarizations, the  $412 \text{ cm}^{-1}$  minimum appeared between  $411$  and  $413 \text{ cm}^{-1}$ , and the  $370 \text{ cm}^{-1}$  minimum appeared between  $372$  and  $368.5 \text{ cm}^{-1}$ . The  $230 \text{ cm}^{-1}$  maximum was comparatively invariant. Fig. 4 shows the polarized reflection spectrum from a (0006) face perpendicular to the optic axis (solid curve). This spectrum is the same in  $N:S$  and  $N:P$  configurations at  $15^\circ$  angle of incidence. On this basis the  $500$  and  $370 \text{ cm}^{-1}$  minima are assigned to the ordinary ray. The broken curve in

Fig. 4 shows the S:S polarized spectrum off the small face inclined  $10^{\circ} 8'$  to the optic axis. In this the  $500 \text{ cm}^{-1}$  minimum is completely missing and the single minimum at  $412 \text{ cm}^{-1}$  appears. This same spectrum is also obtained in the P:P ( $15^{\circ}$ ) configuration and on this basis the  $412 \text{ cm}^{-1}$  minimum is assigned to the extraordinary ray. Additionally, the ordinary ray spectrum was confirmed in the P:S and S:P configurations from this latter face.

At this point, two extraordinary and three ordinary bands are now assigned. However, a fourth ordinary band is expected. The spectral region between  $200$  and  $50 \text{ cm}^{-1}$  was searched using a PE #301 far infrared grating spectrophotometer for additional modes. Powdered ferric oxide blended in polyethylene pellets at both the 10 and 30 weight percent concentrations was examined in transmission but no bands were found. The powder transmission technique was used for this search because it assures reflection bands will not be missed inadvertently by polarization effects and because it allows very weak bands to be sought by control of concentrations. Therefore, the weak band at  $230 \text{ cm}^{-1}$  is assumed to be the remaining fundamental and it is assigned to the ordinary ray on the basis of expectation.

The absolute reflectance spectrum of the ordinary ray is obtained directly from measurements on the (0006) face. The extraordinary ray from a second-order pyramidal face ( $11\bar{2}3$ ) is most nearly isolated when both the optic axis and the electric vector of incident radiation lie in the plane of incidence and the optic axis lies on the reflected beam side. Under these conditions the electric vector is inclined to the optic axis by only about  $27^{\circ}$ . The spectrum of this face with the ordinary ray components pencilled out, is taken to be the absolute reflectance spectrum of the extraordinary ray.

#### DISPERSION ANALYSIS

The multiresonance damped classical oscillator model is used to curve fit the ordinary and extraordinary spectra independently. This theory assumes the

measured reflection spectrum can be approximated by the dielectric properties of a medium containing  $j$  kinds of classical oscillators each described by a resonant frequency, a strength factor, and a damping factor. Following are the definitions of terms and mathematical essentials of this theory:

$$\hat{\epsilon} = \epsilon_{\infty} + \sum_j \frac{\rho_j \nu_j^2}{\nu_j^2 - \omega^2 + i\gamma_j \omega} \quad (1)$$

$$\hat{\epsilon} = \hat{n}^2 = n^2 - 2nk - k^2 \quad (2)$$

$$n^2 - k^2 = \epsilon_{\infty} + \sum_j \frac{\rho_j \nu_j^2 (\nu_j^2 - \omega^2)}{(\nu_j^2 - \omega^2)^2 + \gamma_j^2 \omega^2} \quad (3)$$

$$2nk = \sum_j \frac{\omega \rho_j \gamma_j \nu_j^2}{(\nu_j^2 - \omega^2)^2 + \gamma_j^2 \omega^2} \quad (4)$$

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (5)$$

where

- $\hat{\epsilon}$  = complex dielectric constant
- $\epsilon_{\infty}$  = real dielectric constant at infinitely high frequency
- $\rho_j$  = strength of the  $j$ -th oscillator
- $\nu_j$  = resonant frequency of the  $j$ -th oscillator
- $\omega$  = radiation frequency
- $\gamma_j$  = damping factor of the  $j$ -th oscillator
- $\hat{n}$  = complex refractive index
- $n$  = real refractive index
- $k$  = extinction coefficient
- $R$  = normal incidence reflection coefficient

Equation (5) is modified for non-normal incidence and the attendant polarization effects (Ref 7).

Dispersion analysis is performed by time-shared computation according to the method described in Ref 8. It is performed in real time at an ASR-35 teletype terminal to a remote digital computer. The essential features of this method are: a measured spectrum of 30 or 40 points is entered at the terminal via punched paper tape, a trial solution consisting of assumed sets of oscillator parameters is entered, and the computer then displays a calculated reflectance spectrum superposed over the measured spectrum as a low resolution line printer plot. The quality of fit is judged and a new trial solution is entered, and this process is iterated until further improvements in fit cannot be realized.

High frequency dielectric constants of 8.65 and 10.37 were used for the  $\epsilon$  and  $\omega$  rays, respectively. These are the squares of the refractive indices at the Na D lines for the mineral hematite according to Ref. 9.

The best-fit calculated spectra and the absolute reflectance spectra used for the dispersion analysis are presented in Fig. 5. The resonance parameters associated with these solutions, and estimated accuracies, are presented in Table I. In addition to the 2 fundamentals expected in the  $\epsilon$ -ray spectrum, a "forbidden" mode is found at  $545 \text{ cm}^{-1}$  for which rough values of oscillator parameters have been tabulated. Similarly a forbidden mode at  $590 \text{ cm}^{-1}$  is observed in the  $\omega$ -ray spectrum but its oscillator parameters could not be approximated. Departure from good fit around the  $550$  and  $450 \text{ cm}^{-1}$  reflection maxima of the  $\epsilon$  and  $\omega$  spectra, the  $700 \text{ cm}^{-1}$  reflection minima, and at the shorter wavelengths, are attributed to scattering imperfections of the surface and/or inadequacy of the theory underlying the dispersion equations used.

Accuracies of the best-fit resonance parameters are estimated by studying the degradation of fit as the parameters are changed one at a time. This, of course, is only an approximate method because all of the parameters interact



and influence the fit at any frequency. From Table II it is seen that most of the oscillator frequencies may be located quite accurately even though the bands are broad, while the strength and damping factors can be determined with less certainty.

#### OPTICAL CONSTANT SPECTRA

The various optical and dielectric constant spectra of the  $\epsilon$  and  $\omega$  rays are obtained by reinserting the best-fit resonance parameters into equations (3) and (4) and solving for the refractive index and extinction coefficient at each frequency. From these, the other constants are derived according to the following equations:

$$\text{Absorption coefficient} \quad \alpha = 4\pi vk \quad (6)$$

$$\text{Conductivity} \quad \sigma = v\eta k \quad (7)$$

$$\text{Complex dielectric constant} \quad \hat{\epsilon} = \text{Re}(\epsilon) + i\text{Im}(\epsilon) \quad (8)$$

These values are presented in Tables III, IV, and V and are also plotted in Figs. 6 and 15.

Longitudinal optical phonon frequencies associated with the TO phonons in a multi-resonance spectrum are found by solving for minima in spectrum of the modulus of the complex dielectric constant for each ray, namely

$$|\hat{\epsilon}| = \sqrt{\text{Re}(\epsilon)^2 + \text{Im}(\epsilon)^2}$$

according to Ref 10. These are presented in Table VI. As a point of interest, the LO mode frequencies as would be obtained in a single resonance spectrum by locating the points where  $\text{Re}(\epsilon) = 0$  with positive slope, both with and without damping, are included in this Table.

#### APPLICATION EXAMPLE

Fig. 16 illustrates how data from single crystals may be used as the starting point in the characterization of oxidation film spectra. Shown are the

reflection spectra of thin and thick films of  $\alpha\text{-Fe}_2\text{O}_3$  on pure iron. The thin film was prepared by oxidizing iron in air at  $1400^\circ\text{F}$  for 1 hour. The thick film was in fact a flake which separated from the substrate after heating in air at  $1250^\circ\text{F}$  for 62 hours. From the interference fringe patterns in the transparent region, film thicknesses may be calculated using the refractive index data. The  $700\text{ cm}^{-1}$  reststrahlen minimum is fairly well developed in the thick film spectrum but there is no sign of it in the thin film spectrum. The  $500\text{ cm}^{-1}$   $\omega$ -ray minimum is present in both but it is  $15\text{ cm}^{-1}$  closer to the TO mode frequency in the thin film spectrum. The thin film spectrum shows only the  $\epsilon$ -ray  $412\text{ cm}^{-1}$  minimum, but more complicated structure is found in the thick film spectrum. In addition to the minimum at  $392\text{ cm}^{-1}$ , characteristic of neither ray, weak minima at  $416$  and  $372\text{ cm}^{-1}$  characteristic of both rays are found. This suggests preferential orientation effects in the thick film which may be elucidated with polarization measurements. The  $235\text{ cm}^{-1}$  band is more prominent in the thin film spectrum. With both absorption and reflection processes operating in these spectra a full characterization will require further study. Current work in this laboratory on the oxidation spectra of a variety of alloys indicates that film thickness, grain orientation, measurements and compound identification, and multi-layer film analysis may be performed by this technique.

### REFERENCES

1. Lyon and Phillippi, to be published.
2. Principles of Optics, Born and Wolf, Third Revised Edition, 1965, Pergamon Press.
3. Crystal Structures of Minerals, Bragg, Claringbull, and Taylor, 1965, Cornell University Press.
4. "Raman Effect in Relation to Crystal Structure," Bhagavantam and Venkatarayudu Proc. Indian Acad. Sciences, Vol. 9A, 1939, p244.
5. "Infrared Lattice Vibrations and Dielectric Dispersion in Corundum" A.S. Barker, Jr., Phys. Rev. Vol. 132, Nr 4 15 Nov 1964, p 1414.
6. "Infrared Lattice Vibrations and Dielectric Dispersion in Single-Crystal  $\text{Cr}_2\text{O}_3$ ." Renneke and Lynch, Physical Review, Vol. 138, Nr. 2A, 19 Apr 1965, pA530.
7. Fundamentals of Optics, Jenkins and White, Third Edition, 1957, McGraw-Hill, NY.
8. "Infrared Dispersion Analysis by Time-Shared Computation", Phillippi, AFML-TR-69-256, October 1969.
9. Dana's System of Mineralogy, Palache, Berman, and Frondel, Vol. I, John Wiley & Sons, 7th Edition, 1966.
10. Long-Wavelength Longitudinal Phonons of Multi-Mode Crystals, Chang, Mitra, Plendl, and Mansur, Phys. Stat. Sol., Vol. 28, p 633, 1968.

TABLE I

EMISSION SPECTROGRAPHIC ANALYSIS OF HEMATITE  
AFML/LPA Analysis

<u>Element</u>	<u>Weight Percent</u>
Ti	0.7 to 1.3
Mn	0.06 to 0.1
V	0.01 to 0.03
Al	0.007 to 0.01
Cr	0.001 to 0.003
Co	ND/less than 0.003
Si	ND/less than 0.003
Ni	ND/less than 0.001

TABLE II  
 RESONANCE PARAMETERS OF  $\alpha\text{-Fe}_2\text{O}_3$

RAY	FREQUENCY	STRENGTH	DAMPING
Extraordinary $\epsilon_\infty = 8.65$ forbidden	$510 \pm 1 \text{ cm}^{-1}$	$3 \pm 0.3$	$9 \pm 3 \text{ cm}^{-1}$
	$300 \pm 1$	$15 \pm 0.5$	$15 \pm 3$
	$545 \pm 5$	0.5*	60*
Ordinary $\epsilon_\infty = 10.37$  forbidden	$520 \pm 2$	$1.5 \pm 0.2$	$21 \pm 3$
	$435 \pm 10$	$4.2 \pm 0.3$	$10 \pm 4$
	$297 \pm 5$	$17 \pm 0.5$	$12 \pm 2$
	$235 \pm 2$	$0.6 \pm 0.05$	$3 \pm 0.5$
	590	small	large
* Estimated accurate to within a factor of 2			

TABLE III

OPTICAL CONSTANT SPECTRA OF  $\alpha\text{-Fe}_2\text{O}_3$  IN THE TRANSPARENT REGION

ORDINARY RAY

INPUT HFDC, NR PTS, NR OSC  
8.65, 20, 2,  
INPUT RH0, NU, GAMMA  
15., 300., 15.,  
3., 510., 9.,

FREQ	REFR	IND	EXT	C0EF	ABS C0EF	C0ND TY	RE(D.C.)	IM(D.C.)
4000.0	2.918			.000	3.72	.86	8.52	.00
3750.0	-2.915			.000	4.25	.99	8.50	.00
3500.0	2.911			.000	4.91	1.14	8.47	.00
3250.0	2.906			.000	5.72	1.32	8.45	.00
3000.0	2.900			.000	6.76	1.56	8.41	.00
2750.0	2.892			.000	8.12	1.87	8.36	.00
2500.0	2.881			.000	9.94	2.28	8.30	.00
2250.0	2.866			.000	12.47	2.84	8.22	.00
2000.0	2.845			.001	16.13	3.65	8.10	.00
1800.0	2.821			.001	20.43	4.59	7.96	.01
1600.0	2.786			.001	26.82	5.95	7.76	.01
1400.0	2.733			.002	37.04	8.06	7.47	.01
1200.0	2.644			.004	55.28	11.63	6.99	.02
1000.0	2.472			.008	94.73	18.64	6.11	.04
950.0	2.403			.009	112.51	21.52	5.77	.05
900.0	2.315			.012	136.92	25.22	5.36	.06
850.0	2.198			.016	172.34	30.14	4.83	.07
800.0	2.036			.023	228.26	36.98	4.14	.09
750.0	1.793			.035	329.90	47.08	3.22	.13
700.0	1.375			.066	580.55	63.52	1.89	.18

EXTRAORDINARY RAY

INPUT HFDC, NR PTS, NR OSC  
10.37, 20, 4,  
INPUT RH0, NU, GAMMA  
17., 297., 12.,  
4.2, 435., 10.,  
1.5, 520., 21.,  
.6, 235., 3.,

FREQ	REFR	IND	EXT	C0EF	ABS C0EF	C0ND TY	RE(D.C.)	IM(D.C.)
4000.0	3.193			.000	4.33	1.10	10.20	.00
3750.0	3.190			.000	4.94	1.25	10.17	.00
3500.0	3.185			.000	5.71	1.45	10.14	.00
3250.0	3.179			.000	6.66	1.68	10.11	.00
3000.0	3.172			.000	7.88	1.99	10.06	.00
2750.0	3.163			.000	9.47	2.38	10.00	.00
2500.0	3.150			.000	11.61	2.91	9.92	.00
2250.0	3.133			.001	14.59	3.64	9.81	.00
2000.0	3.108			.001	18.94	4.68	9.66	.00
1800.0	3.080			.001	24.06	5.90	9.49	.01
1600.0	3.039			.002	31.75	7.68	9.24	.01
1400.0	2.977			.003	44.18	10.47	8.86	.01
1200.0	2.873			.004	66.77	15.26	8.25	.03
1000.0	2.675			.009	117.04	24.91	7.16	.05
950.0	2.595			.012	140.25	28.96	6.73	.06
900.0	2.494			.015	172.54	34.24	6.22	.08
850.0	2.360			.021	220.18	41.36	5.57	.10
800.0	2.177			.030	296.82	51.42	4.74	.13
750.0	1.906			.047	439.25	66.63	3.63	.18
700.0	1.446			.091	799.50	92.02	2.08	.26

TABLE IV

OPTICAL CONSTANT SPECTRA OF  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> U-RAY IN THE RESTRAHLEN REGION

INPUT HFDC, NR PIS, NR BSC

10.37, 54, 4,

INPUT RH0, NU, GAMMA

17., 297., 12.,

4.2, 435., 10.,

1.5, 520., 21.,

.6, 235., 3.,

FREQ	REFR	IND	EXT	COEF	ABS COEF	COND TY	RE(D.C.)	IM(D.C.)
700.0	1.446			.091	799.50	92.02	2.08	.26
690.0	1.307			.110	954.21	99.25	1.70	.29
680.0	1.138			.139	1188.31	107.57	1.27	.32
670.0	.922			.190	1598.24	117.24	.61	.35
660.0	.634			.307	2550.25	128.61	.31	.39
650.0	.355			.616	5030.24	142.14	-.25	.44
640.0	.255			.971	7805.55	158.50	-.88	.50
630.0	.222			1.275	10095.96	178.64	-1.58	.57
620.0	.212			1.554	12107.72	203.98	-2.37	.66
610.0	.213			1.824	13978.55	236.68	-3.28	.78
600.0	.223			2.095	15795.71	280.27	-4.34	.93
590.0	.243			2.378	17629.30	340.73	-5.59	1.16
580.0	.276			2.682	19551.33	428.99	-7.12	1.48
570.0	.329			3.023	21653.11	566.76	-9.03	1.99
560.0	.419			3.420	24069.89	802.39	-11.52	2.87
550.0	.586			3.910	27021.41	1259.87	-14.94	4.58
540.0	.946			4.544	30835.31	2322.29	-19.75	8.60
530.0	1.894			5.289	35223.55	5310.25	-24.38	20.04
520.0	3.942			4.826	31538.15	9893.04	-7.76	38.05
510.0	4.001			2.598	16648.85	5301.06	9.26	20.79
500.0	2.633			1.805	11340.46	2375.86	3.67	9.50
490.0	1.339			2.222	13680.16	1457.68	-3.14	5.95
480.0	.781			3.235	19513.46	1212.17	-9.86	5.05
470.0	.667			4.269	25214.11	1338.40	-17.78	5.70
460.0	.791			5.473	31639.03	1990.44	-29.33	8.65
450.0	1.354			7.254	41018.82	4418.70	-50.78	19.64
440.0	4.420			10.426	57648.04	20276.56	-89.17	92.17
435.0	9.599			9.586	52399.10	40024.94	.25	184.02
430.0	10.548			4.418	23871.84	20037.96	91.75	93.20
420.0	7.426			1.326	7000.64	4137.18	53.39	19.70
410.0	5.669			.752	3873.04	1747.14	31.57	8.52
400.0	4.468			.596	2995.78	1065.10	19.61	5.33
390.0	3.412			.612	2998.06	814.06	11.27	4.17
380.0	2.243			.858	4099.20	731.81	4.30	3.85
370.0	1.067			1.891	8792.98	746.58	-2.44	4.04
360.0	.733			3.209	14517.37	846.55	-9.76	4.70
350.0	.692			4.367	19207.47	1057.64	-18.59	6.04
340.0	.773			5.563	23768.95	1462.84	-30.35	8.60
330.0	.996			6.983	28959.25	2294.36	-47.78	13.91
320.0	1.519			8.919	35865.17	4334.44	-77.24	27.09
310.0	3.065			12.019	46822.78	11421.28	-135.07	73.69
300.0	10.452			15.990	60281.64	50136.77	-146.45	334.25
297.0	14.849			14.179	52918.81	62531.03	19.45	421.08
290.0	16.200			5.565	20279.44	26142.90	231.47	180.30
280.0	12.592			1.873	6589.83	6603.04	155.04	47.16
270.0	10.585			.952	3228.72	2719.58	111.13	20.15
260.0	9.366			.594	1941.39	1446.92	87.36	11.13
250.0	8.474			.434	1362.84	919.05	71.63	7.35
240.0	7.378			.583	1757.29	1031.73	54.09	8.60
235.0	8.504			2.999	8856.61	5993.19	63.32	51.01
230.0	8.576			.427	1234.52	842.54	73.37	7.33
220.0	7.758			.198	548.48	338.63	60.15	3.08
210.0	7.383			.150	396.41	232.91	54.49	2.22
200.0	7.118			.122	306.07	173.38	50.66	1.73

TABLE V  
OPTICAL CONSTANT SPECTRA OF  $\alpha\text{-Fe}_2\text{O}_3$  c-RAY IN THE RESTRAHLEN REGION

INPUT HFDC, NR PTS, NR OSC  
8.65, 54, 2,  
INPUT RHO, NU, GAMMA  
15., 300., 15.,  
3., 510., 9.,

FREQ	REFR	IND	EXT	COEF	ABS COEF	COND TY	RE(D.C.)	IM(D.C.)
700.0	1.375			.066	580.55	63.52	1.89	.18
690.0	1.246			.079	686.91	68.12	1.55	.20
680.0	1.088			.099	847.42	73.37	1.17	.22
670.0	.884			.134	1129.70	79.43	.76	.24
660.0	.595			.220	1826.00	86.50	.31	.26
650.0	.275			.530	4329.88	94.84	-.21	.29
640.0	.181			.903	7259.68	104.82	-.78	.33
630.0	.154	1.209			9573.79	116.97	-1.44	.37
620.0	.143	1.489			11599.22	132.05	-2.20	.43
610.0	.141	1.761			13497.79	151.20	-3.08	.50
600.0	.144	2.038			15365.89	176.24	-4.13	.59
590.0	.153	2.331			17280.93	210.11	-5.41	.71
580.0	.168	2.651			19323.92	257.99	-7.00	.89
570.0	.192	3.015			21599.22	329.54	-9.06	1.16
560.0	.230	3.448			24264.37	444.75	-11.84	1.59
550.0	.296	3.992			27591.63	650.62	-15.85	2.37
540.0	.423	4.734			32123.52	1080.44	-22.23	4.00
530.0	.720	5.879			39158.36	2243.81	-34.05	8.47
520.0	1.792	8.051			52611.60	7502.14	-61.61	28.85
510.0	9.249	9.209			59022.17	43440.83	.73	170.36
500.0	8.235	1.768			11107.03	7278.75	64.69	29.11
490.0	6.114	.707			4352.29	2117.61	36.88	8.64
480.0	4.997	.424			2555.61	1016.19	24.79	4.23
470.0	4.259	.314			1856.10	629.12	18.04	2.68
460.0	3.692	.270			1559.05	458.01	13.56	1.99
450.0	3.200	.260			1471.30	374.68	10.17	1.67
440.0	2.728	.279			1543.49	355.07	7.36	1.52
435.0	2.484	.301			1647.36	325.63	6.08	1.50
430.0	2.225	.336			1815.15	321.42	4.84	1.49
420.0	1.625	.478			2523.17	326.23	2.41	1.55
410.0	.903	.937			4825.81	346.94	-.06	1.69
400.0	.553	1.737			8729.19	384.20	-2.71	1.92
390.0	.466	2.429			11902.10	441.57	-5.68	2.26
380.0	.453	3.060			14612.09	526.52	-9.16	2.77
370.0	.478	3.693			17169.84	653.11	-13.41	3.53
360.0	.539	4.374			19788.18	848.21	-18.84	4.71
350.0	.647	5.156			22676.58	1167.10	-26.16	6.67
340.0	.836	6.113			26119.50	1737.22	-36.67	10.22
330.0	1.193	7.380			30602.43	2905.31	-53.03	17.61
320.0	1.992	9.223			37086.03	5878.71	-81.09	36.74
310.0	4.417	12.086			47083.57	16551.23	-126.57	106.78
300.0	12.522	11.982			45170.54	45010.92	13.24	300.07
297.0	14.221	9.174			34241.23	38749.47	118.06	260.94
290.0	13.346	4.097			14931.03	15856.78	161.32	109.36
280.0	10.898	1.712			6023.60	5223.84	115.83	37.31
270.0	9.405	.944			3203.19	2397.47	87.57	17.76
260.0	8.460	.605			1976.23	1330.37	71.20	10.23
250.0	7.808	.424			1331.11	827.12	60.79	6.62
240.0	7.332	.315			948.99	553.71	53.66	4.61
235.0	7.139	.276			813.79	462.29	50.88	3.93
230.0	6.968	.243			703.59	390.13	48.49	3.39
220.0	6.680	.194			536.51	285.20	44.58	2.59
210.0	6.447	.158			417.65	214.26	41.54	2.04
200.0	6.254	.131			330.16	164.32	39.10	1.64



TABLE VI  
 LONGITUDINAL OPTICAL PHONON FREQUENCIES OF  $\alpha\text{-Fe}_2\text{O}_3$

RAY	TO MODE	LO MODE <sup>1</sup>	LO MODE <sup>2</sup>	LO MODE <sup>3</sup>
$\epsilon$	510 $\text{cm}^{-1}$	655 $\text{cm}^{-1}$	654 $\text{cm}^{-1}$	654 $\text{cm}^{-1}$
	300	410.6	410.5	410.2
$\omega$	520	655	654.5	654.5
	435	491.5	492.5	494.7
	297	373.7	373.5	373.6
	235	237.2	236.1	236.4 <sup>4</sup>

Notes:

- 1) Frequencies of minima in the spectra of the modulus of the complex dielectric constant
- 2) Frequencies of zeroes in the spectra of the real part of the dielectric constant, assuming zero damping for each resonance
- 3) Frequencies of zeroes in the spectra of the real part of the dielectric constant, using the damping factors for each resonance found in the best fit solution
- 4) No zero; this is the frequency of the minimum

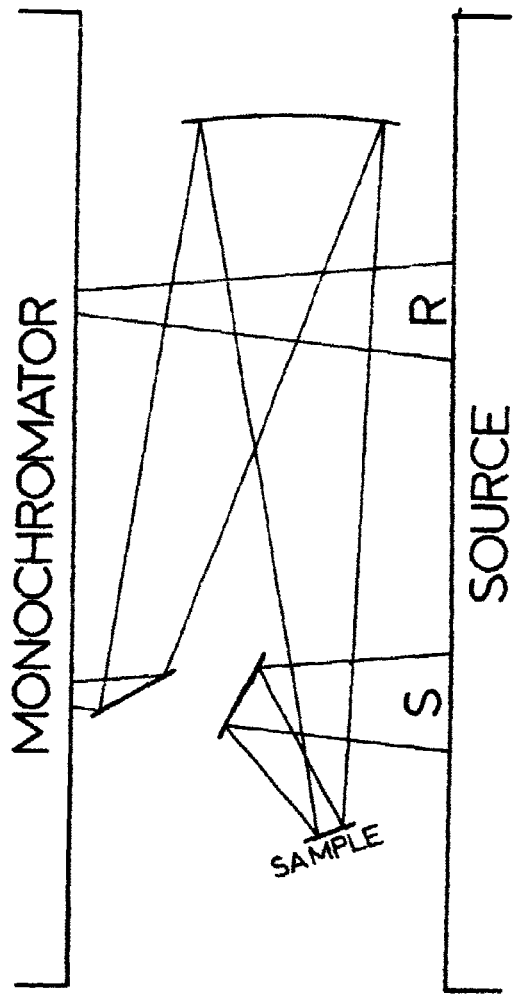
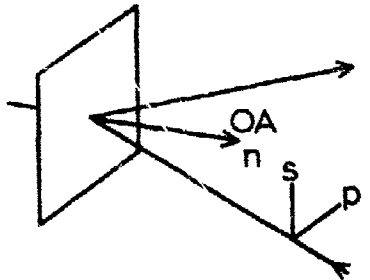
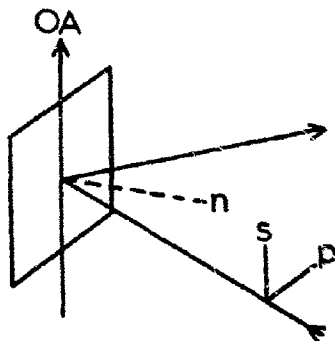


Fig. 1. Specular Reflectance Attachment for PE #225  
Sample Compartment

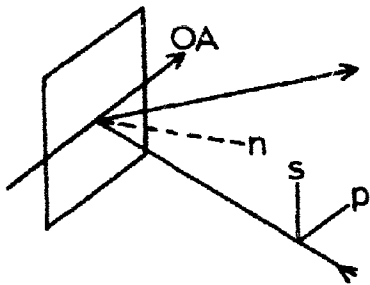
# UNIAXIAL CRYSTAL REFLECTION SPECTRA



N:S



S:S



S:P

P:S

P:P

OPTIC AXIS	POLARIZATION	INCIDENCE		
		NORMAL	INTER-MEDIATE	GRAZING
N	s	⊥	⊥	⊥
N	p	⊥	mix	
S	s			
S	p	⊥	⊥	⊥
P	s	⊥	⊥	⊥
P	p		mix	⊥

N=Optic Axis normal to surface  
 P=p=Parallel to plane of inc.  
 S=s=Perp'r to plane of inc.  
 || = EIC vibration  
 ⊥ = EIC vibration

Fig. 2. Optical Geometry for Isolating Ordinary and Extraordinary Ray Spectra of Uniaxial Crystals

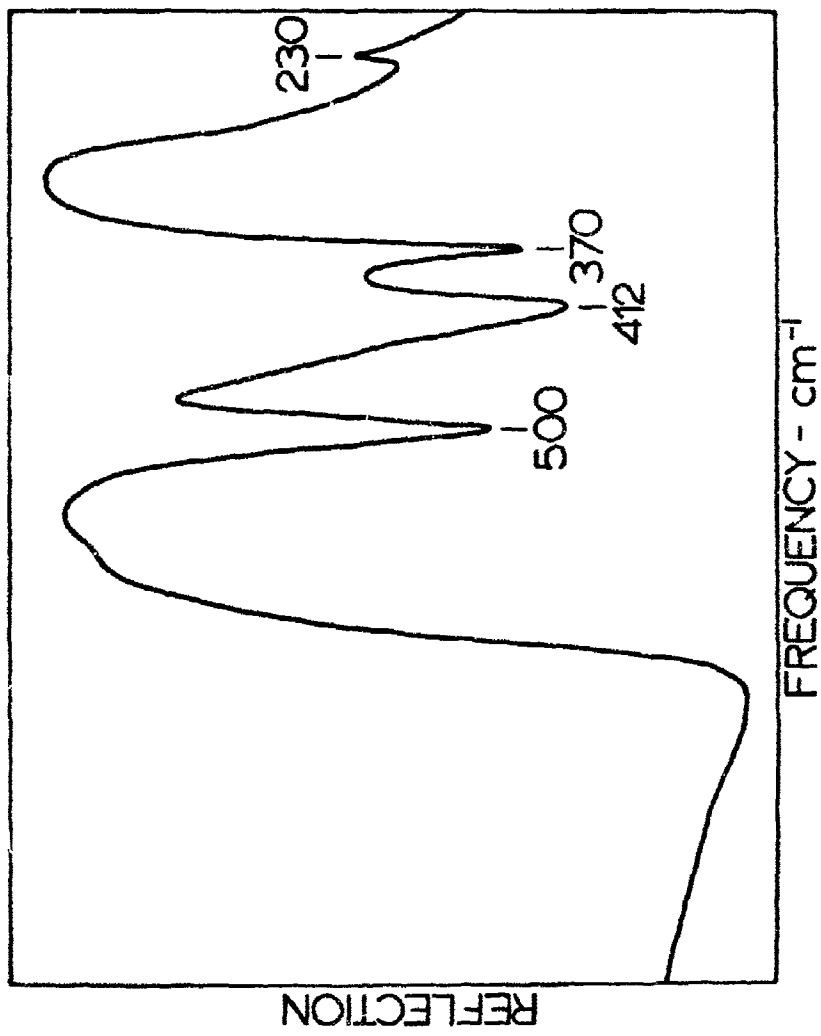


Fig. 3. Unpolarized Reflection Spectrum From Pyramidal Face of Hematite

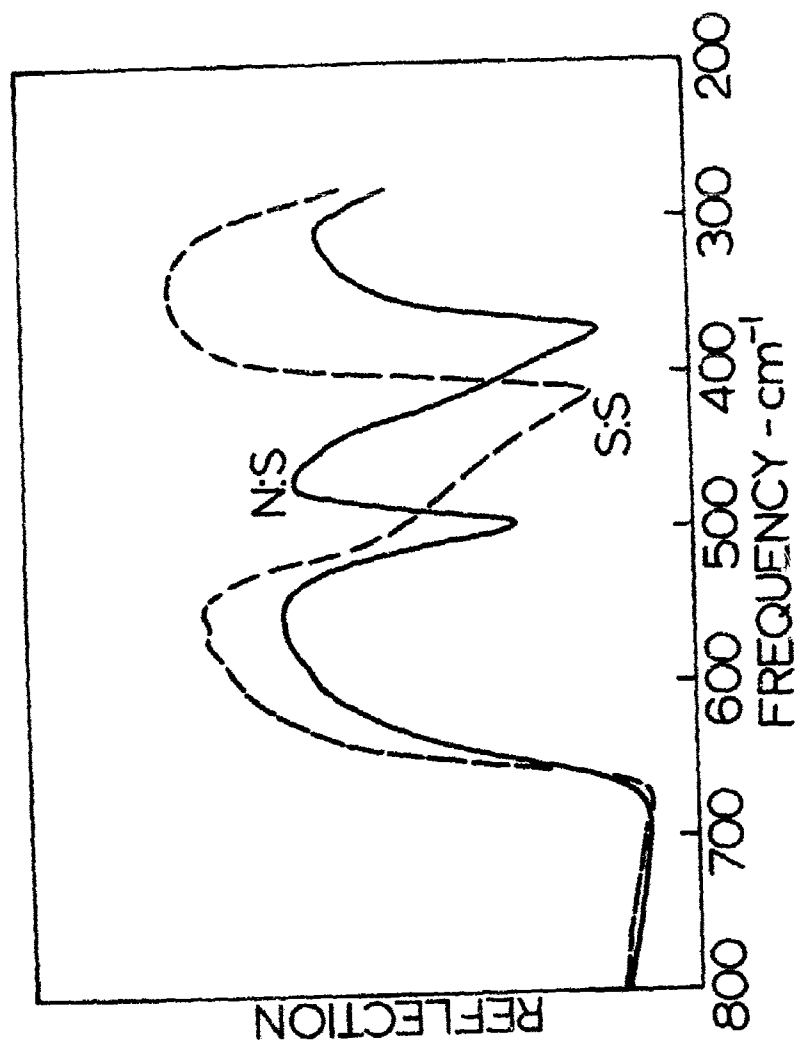


Fig. 4. Ordinary and Extraordinary Reflection Spectra of Hematite

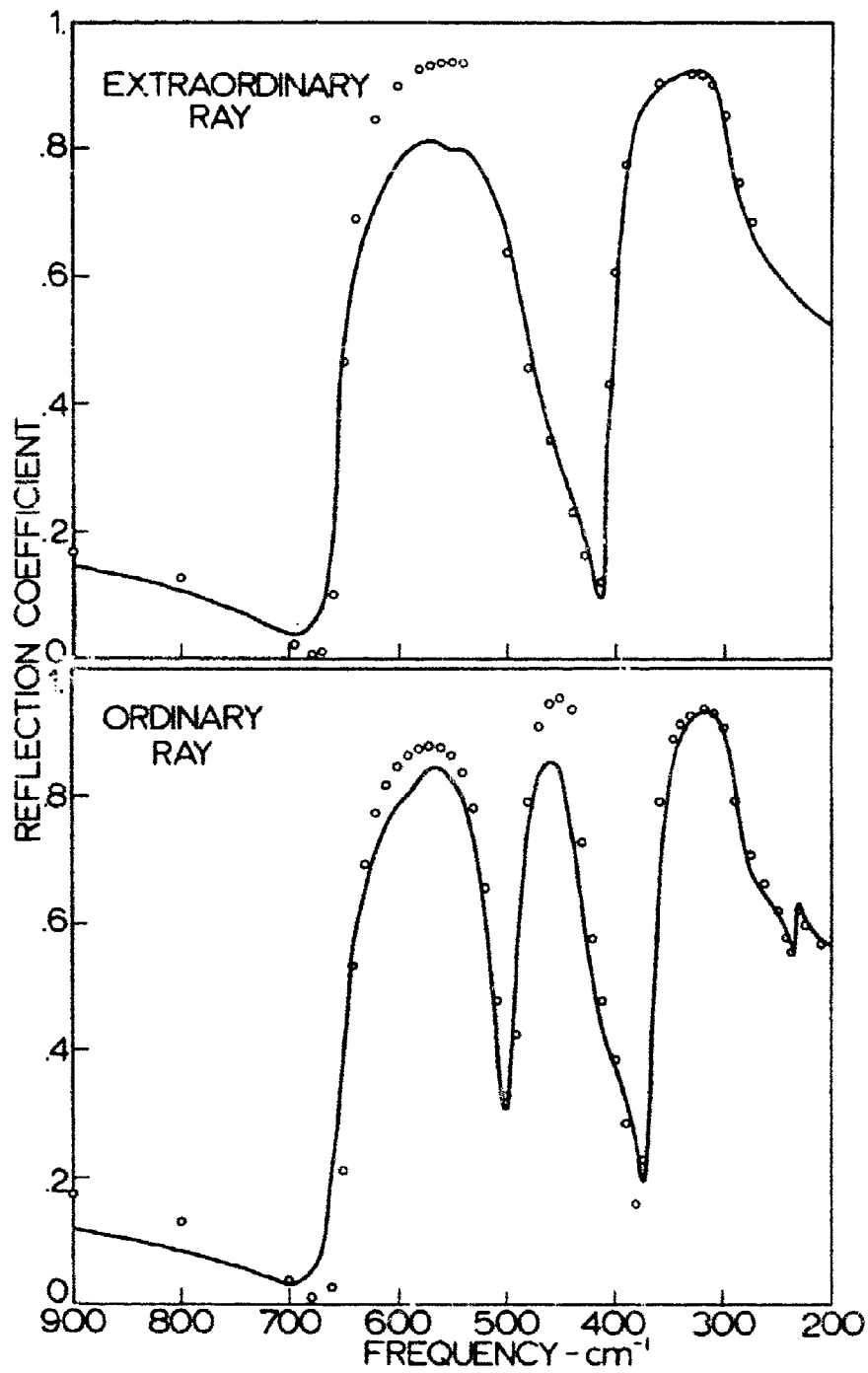


Fig. 5. Measured (Solid Line) and Best Fit Calculated (Circles) Ordinary and Extraordinary Reflection Spectra of Hematite

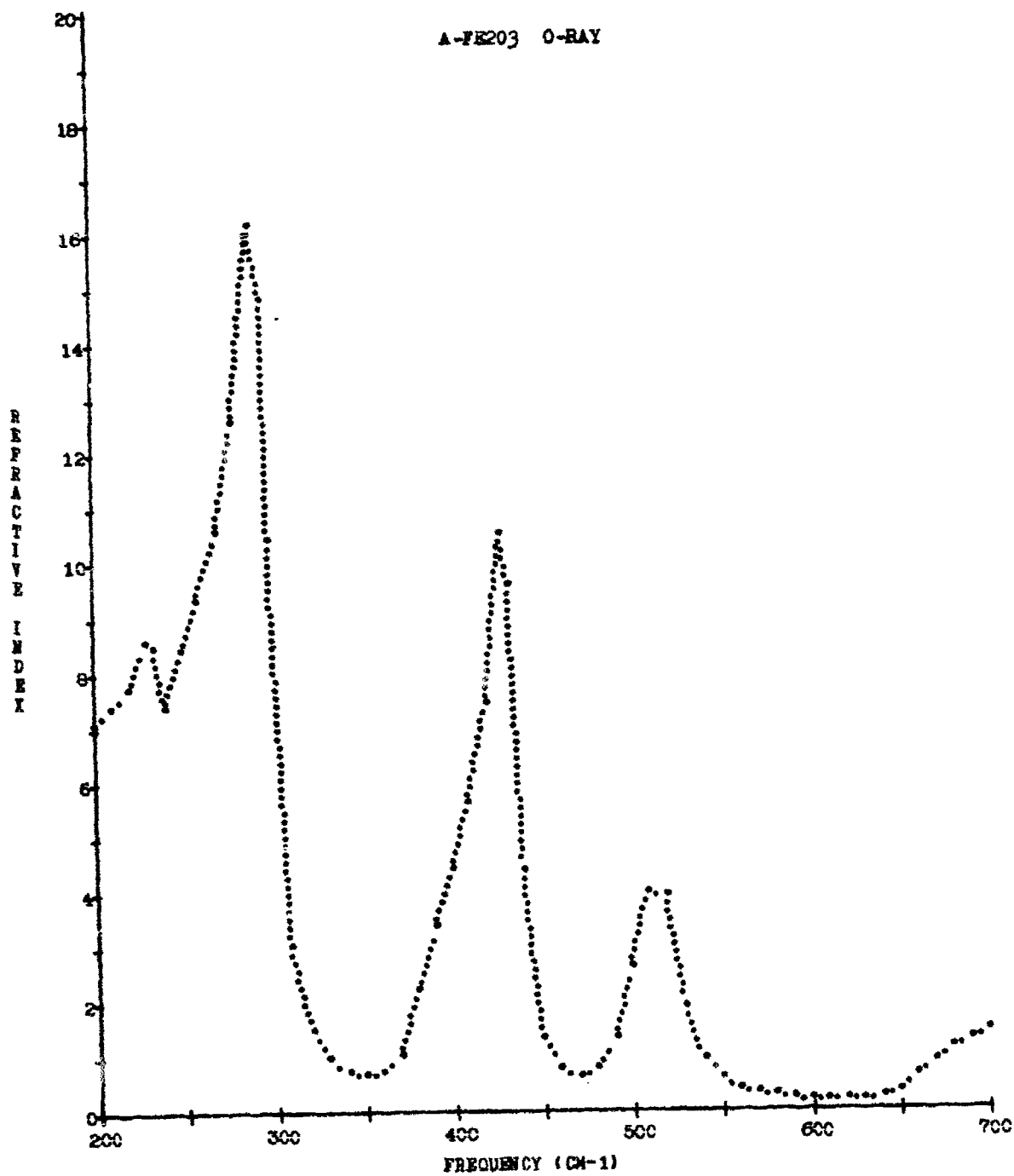


Fig. 6. Refractive Index Spectrum of Ordinary Ray of Hematite

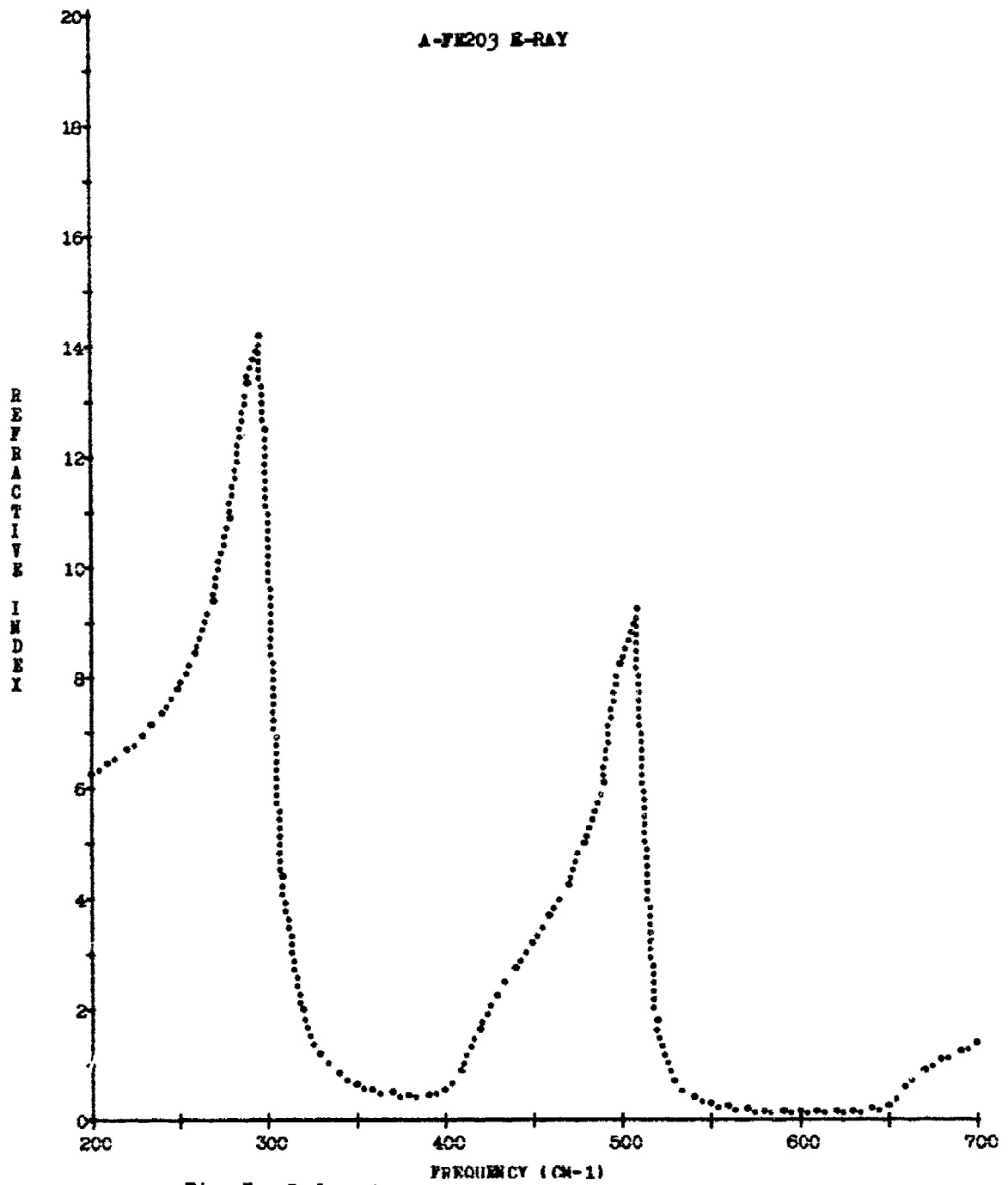


Fig. 7. Refractive Index Spectrum of Extraordinary Ray of Hematite



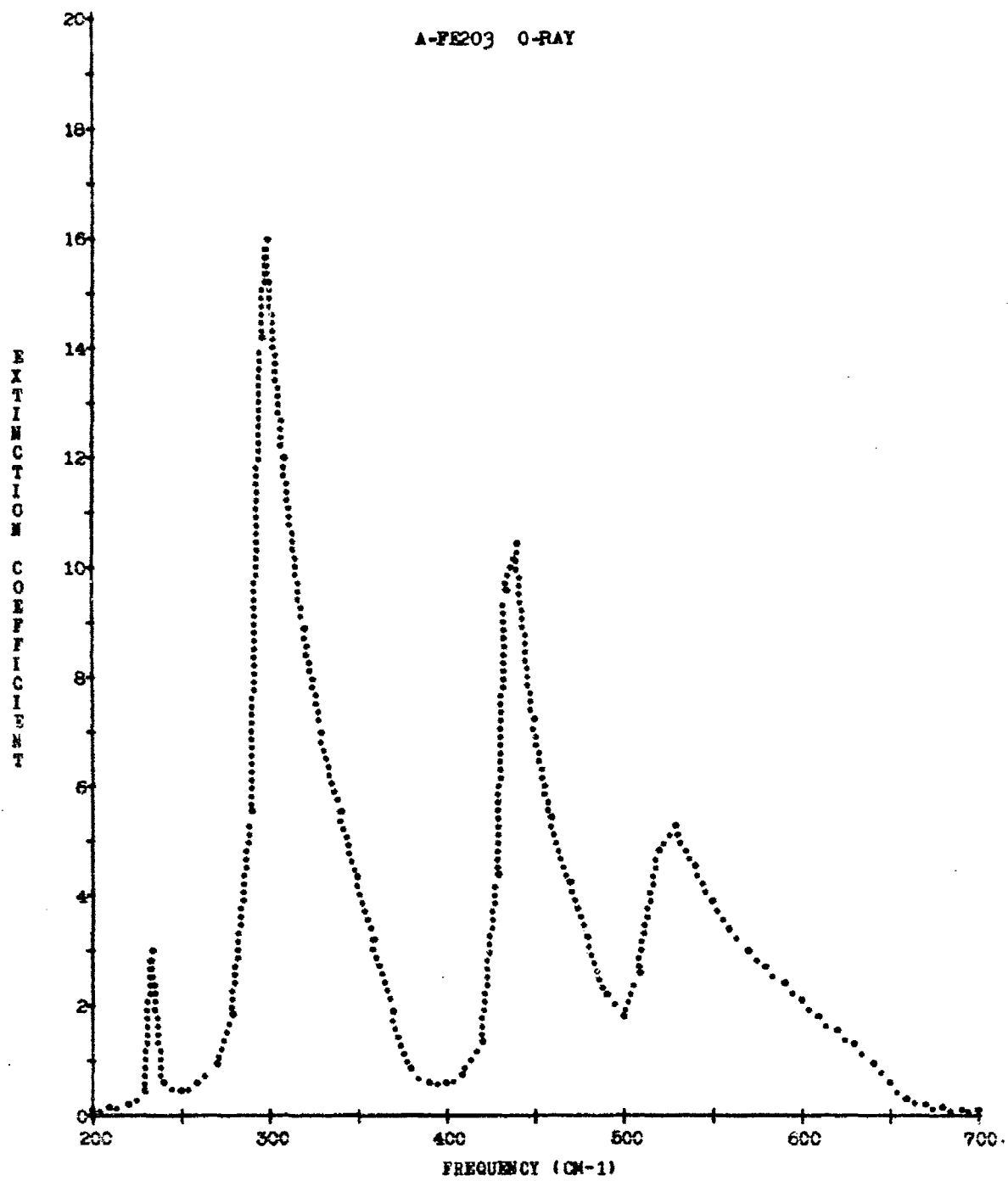


Fig. 8. Extinction Coefficient Spectrum of Ordinary Ray of Hematite

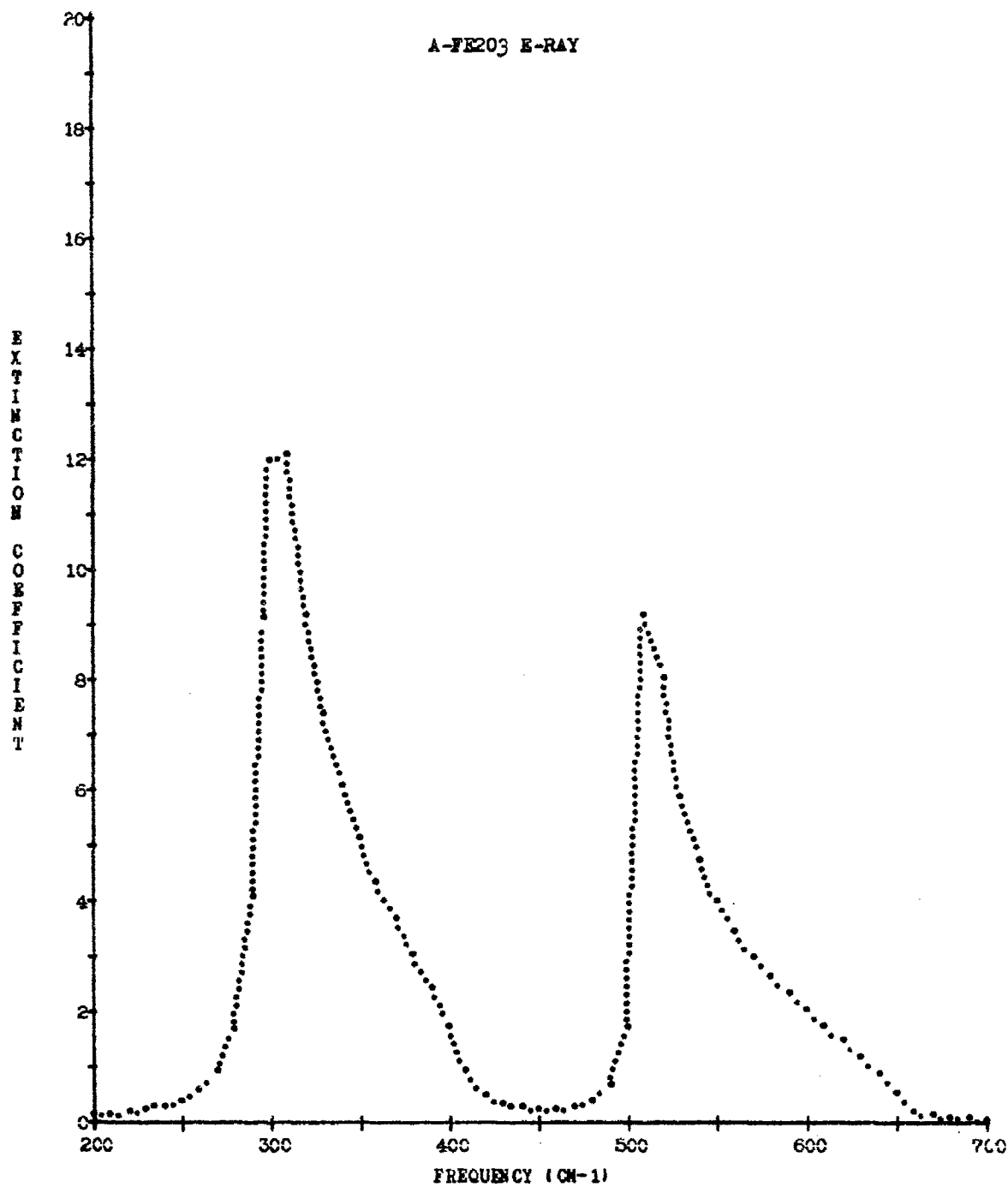


Fig. 9. Extinction Coefficient Spectrum of Extraordinary Ray of Hematite

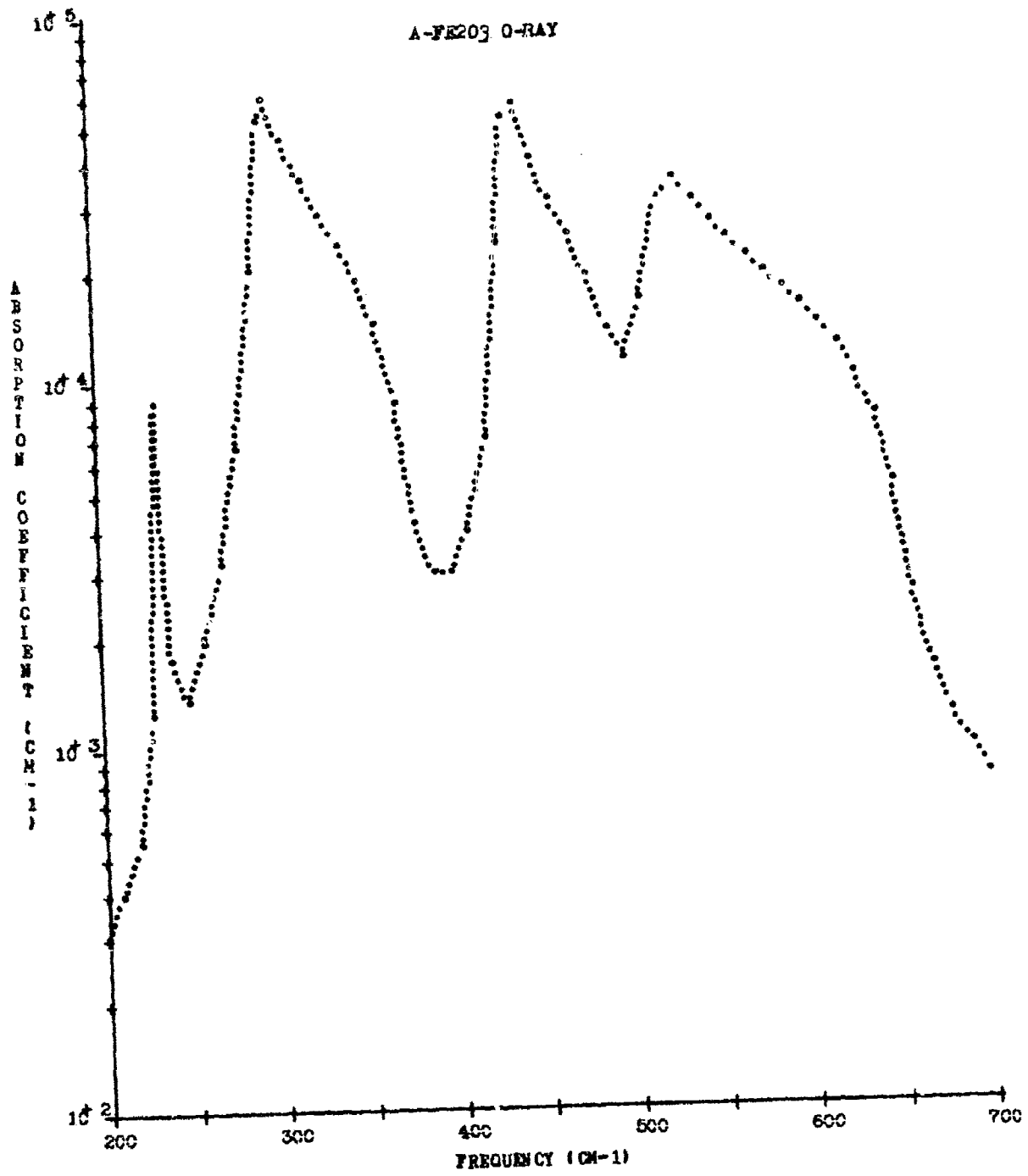


Fig. 10. Absorption Coefficient Spectrum of Ordinary Ray of Hematite

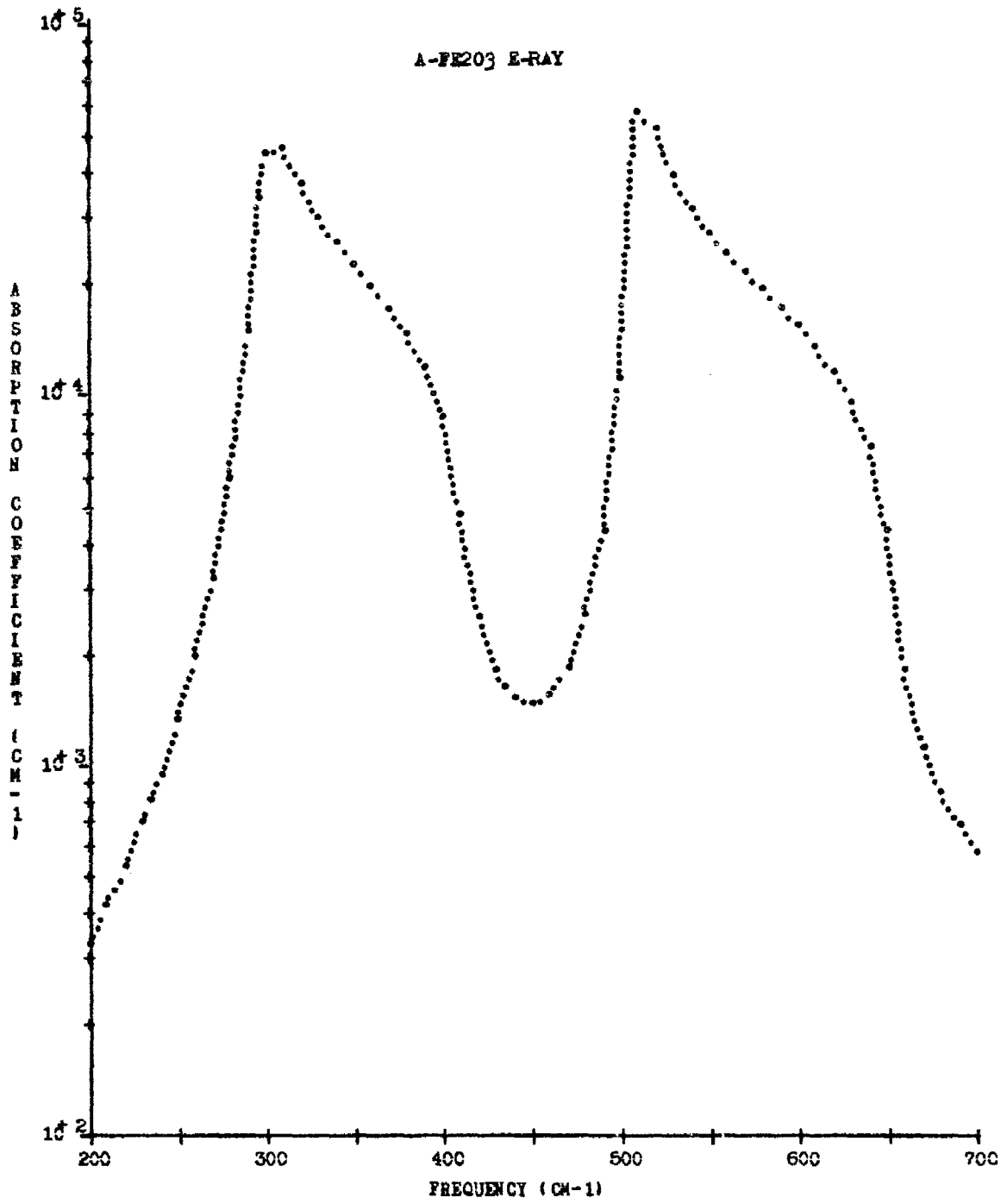


Fig. 11. Absorption Coefficient Spectrum of Extraordinary Ray of Hematite

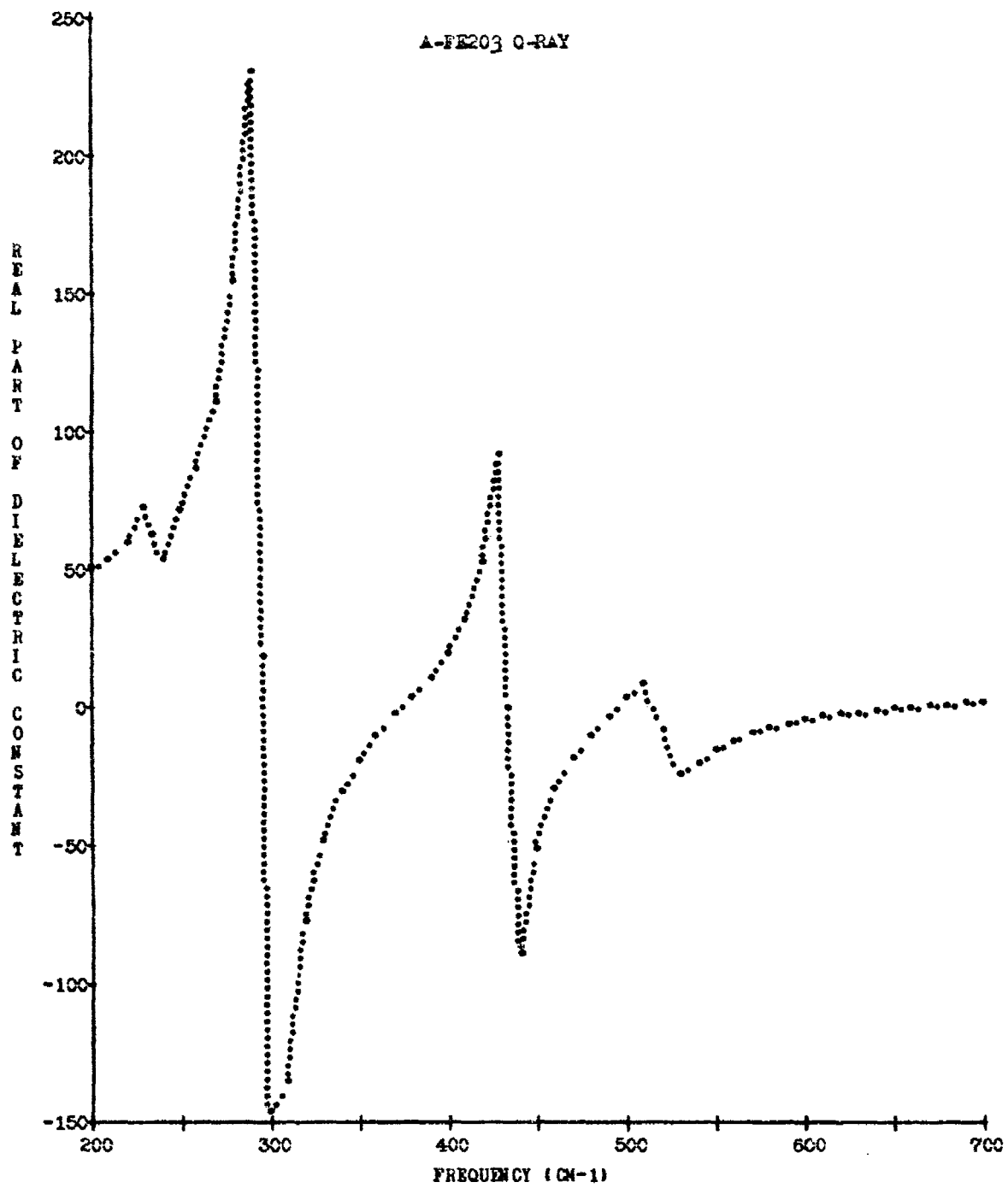


Fig. 12. Spectrum of the Real Part of the Dielectric Constant of Ordinary Ray of Hematite

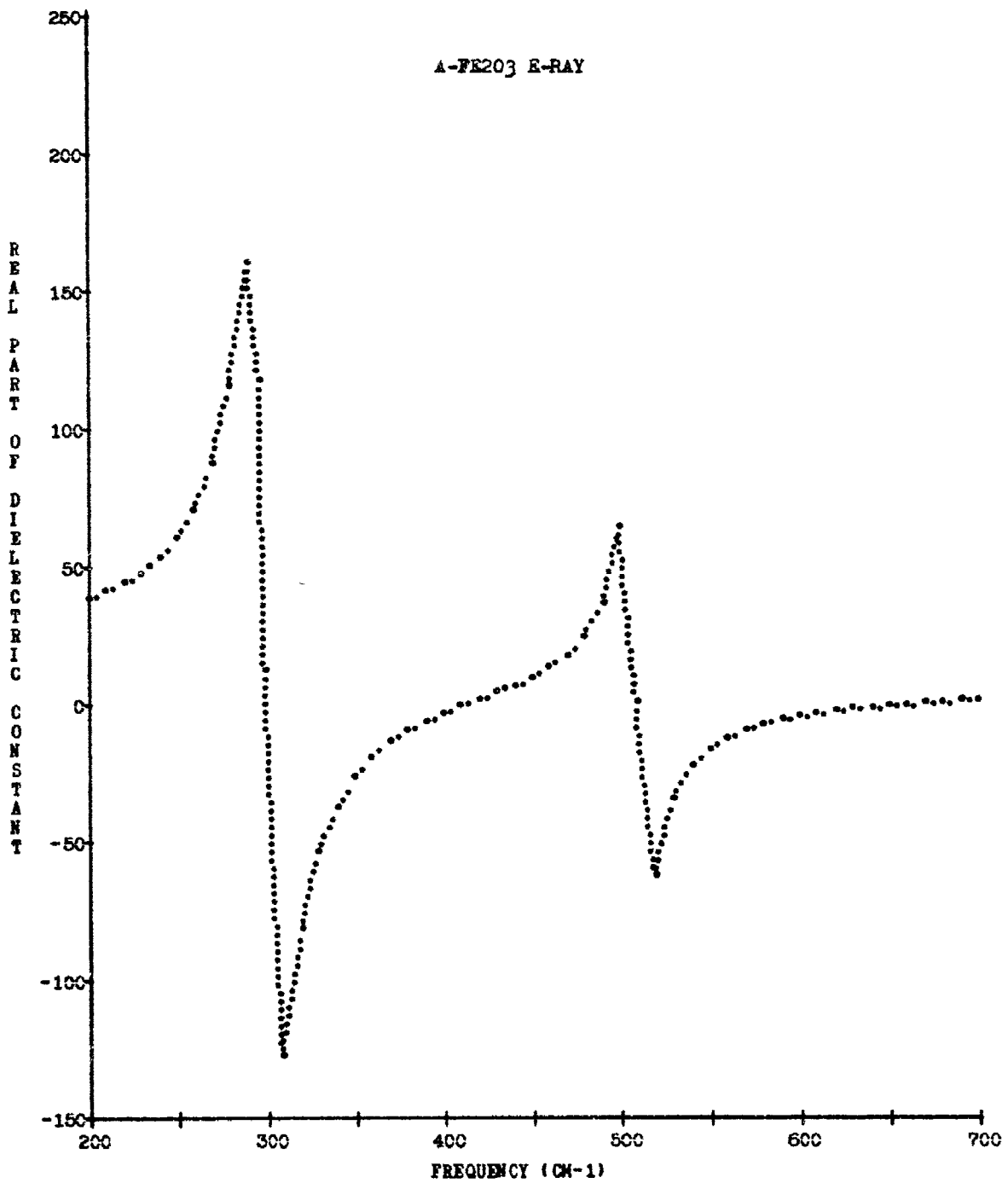


Fig. 13. Spectrum of the Real Part of the Dielectric Constant of Extraordinary Ray of Hematite

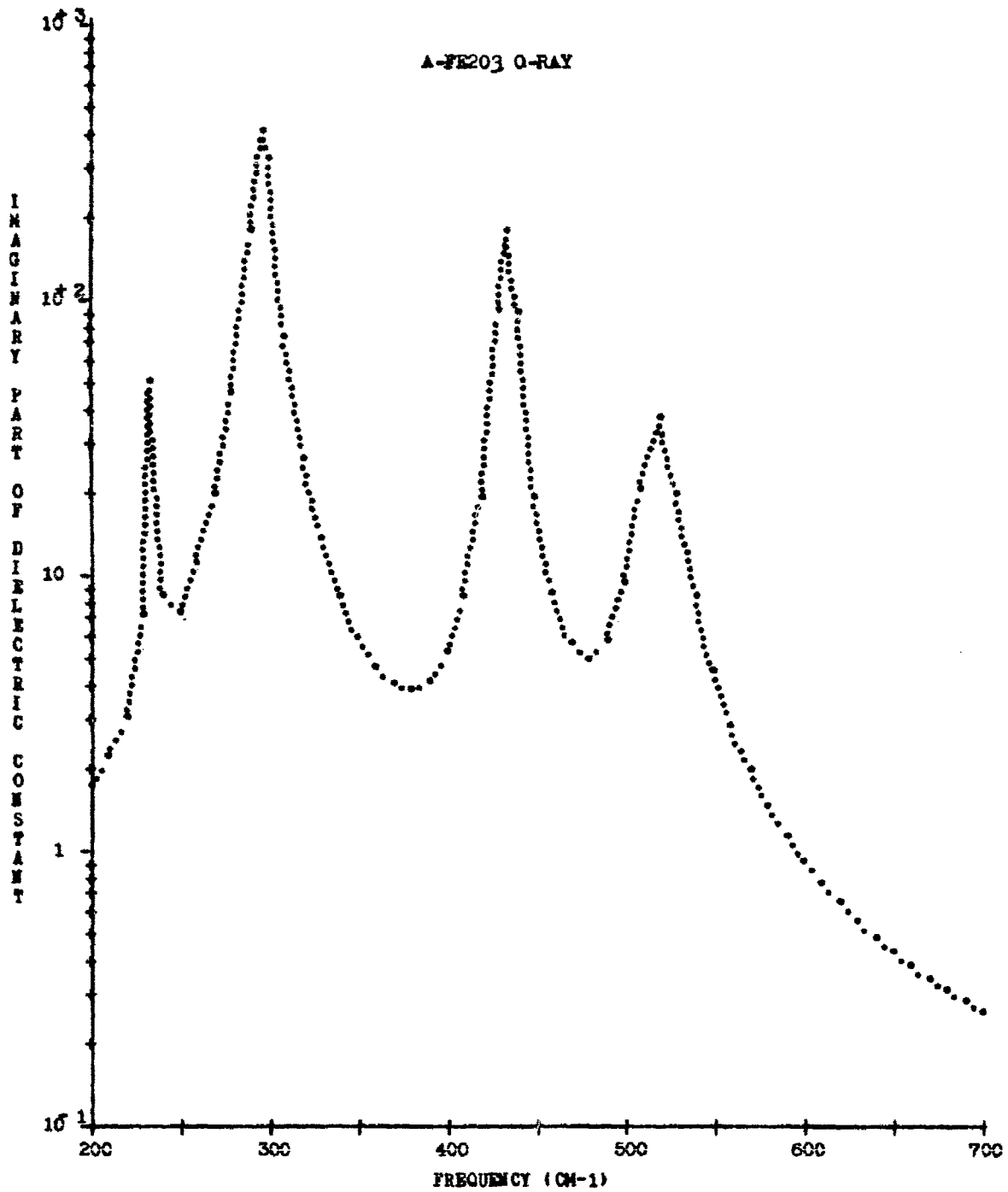


Fig. 14. Spectrum of the Imaginary Part of the Dielectric Constant of Ordinary Ray of Hematite

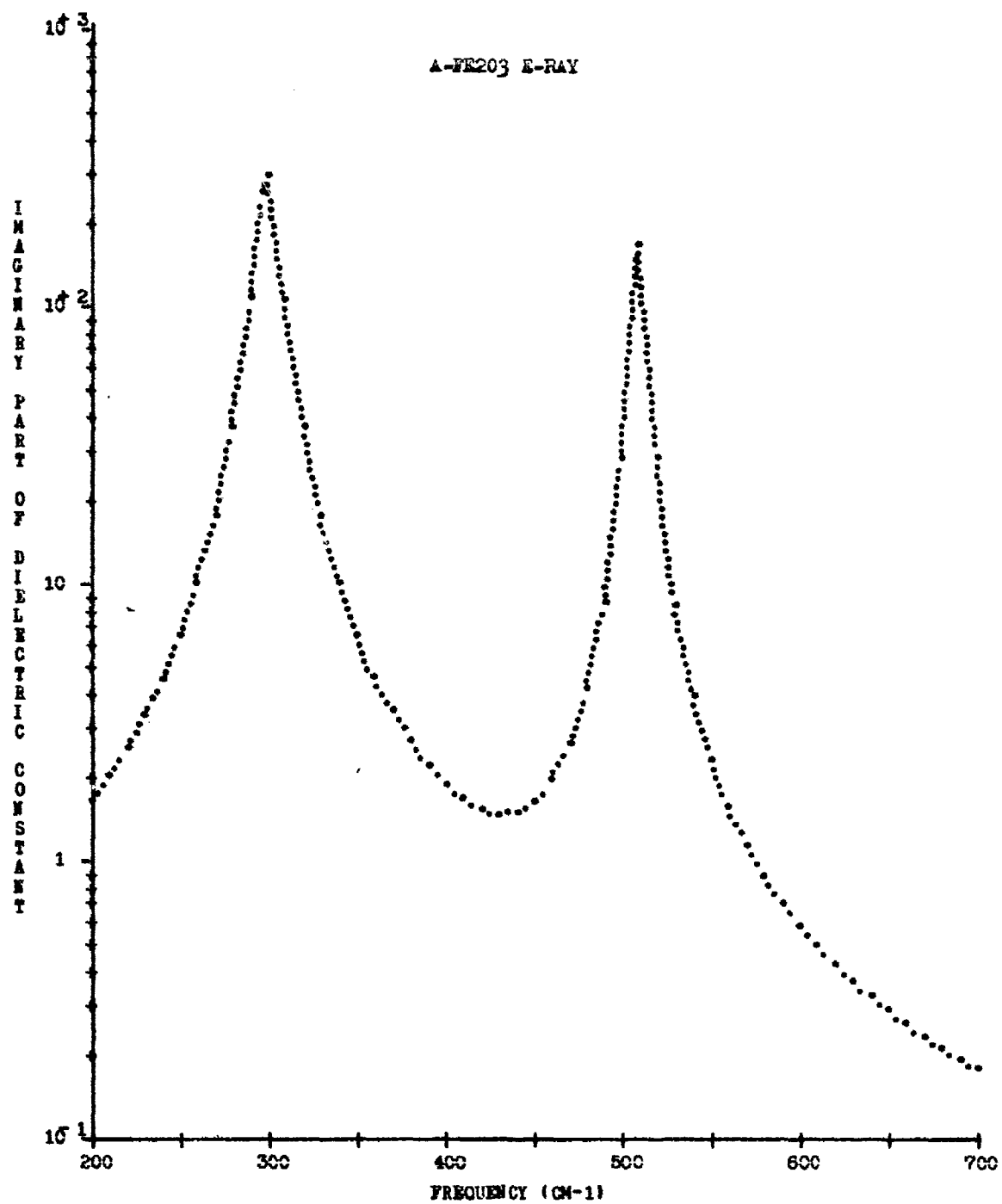


Fig. 15. Spectrum of the Imaginary Part of the Dielectric Constant of Extraordinary Ray of Hematite



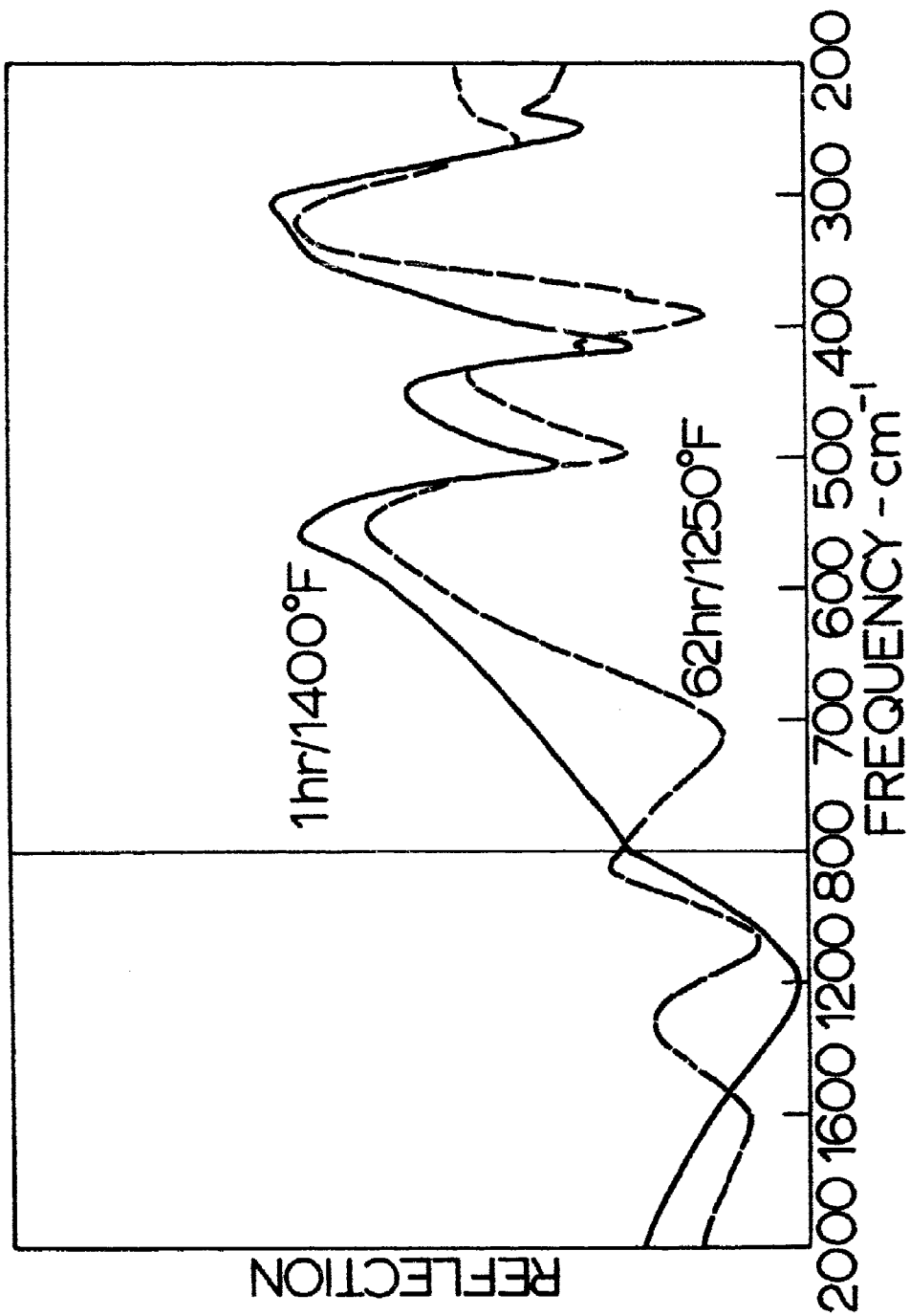


Fig. 16. Reflection Spectra of Oxidation Films on Pure Iron