

5-20-1953

The Crystal Structure of CeNi

Joseph J. Finney

Follow this and additional works at: https://digitalrepository.unm.edu/eps_etds



Part of the [Geology Commons](#), [Hydrology Commons](#), and the [Other Earth Sciences Commons](#)

Recommended Citation

Finney, Joseph J.. "The Crystal Structure of CeNi." (1953). https://digitalrepository.unm.edu/eps_etds/144

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at UNM Digital Repository. It has been accepted for inclusion in Earth and Planetary Sciences ETDs by an authorized administrator of UNM Digital Repository. For more information, please contact disc@unm.edu.

UNIVERSITY OF NEW MEXICO-UNIVERSITY LIBRARIES



A14429 120993

378.789

Un30fi

1959

cop. 2

FRYSTAL STAFF OF CELESTINE - FINNEY

THE LIBRARY
UNIVERSITY OF NEW MEXICO

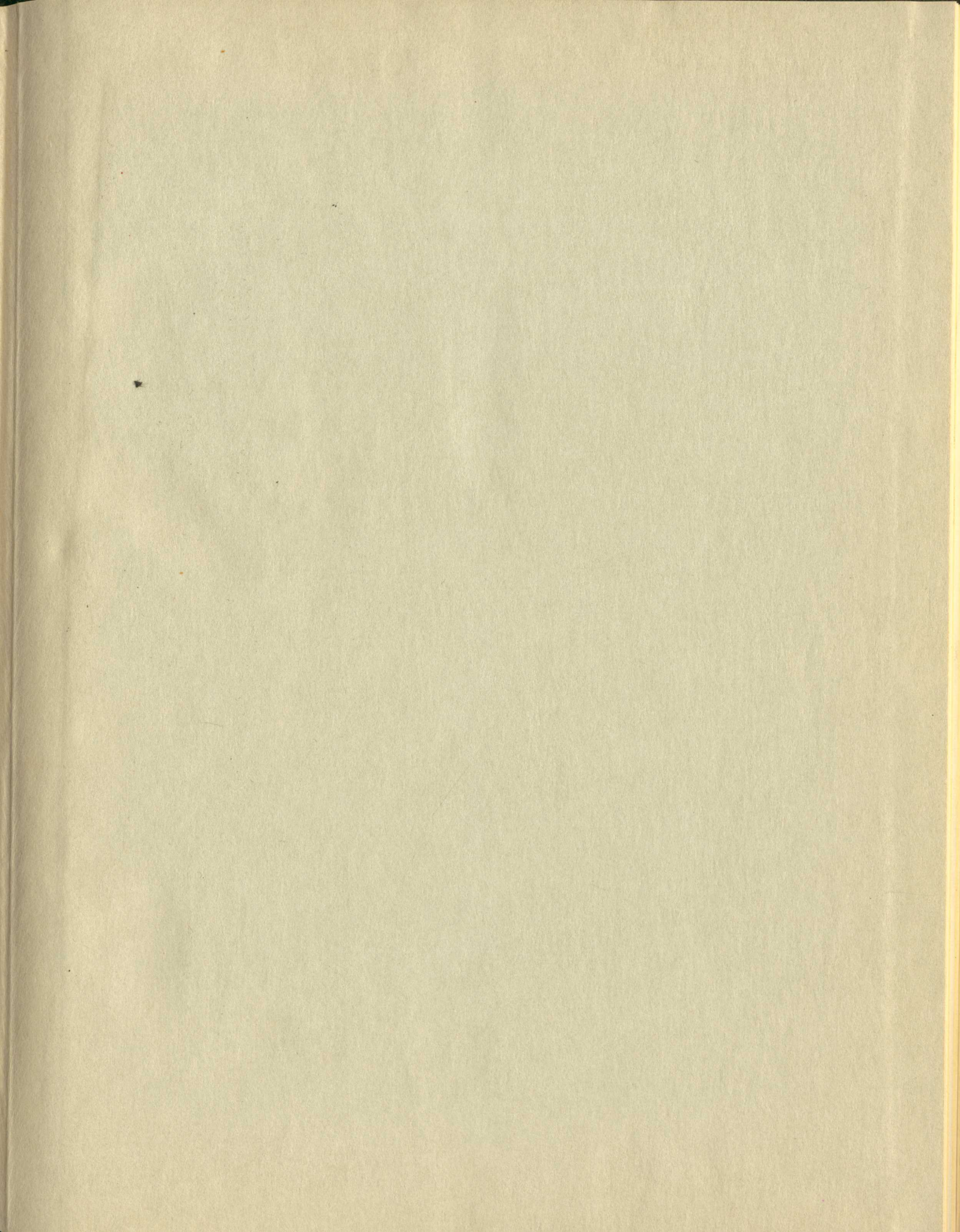


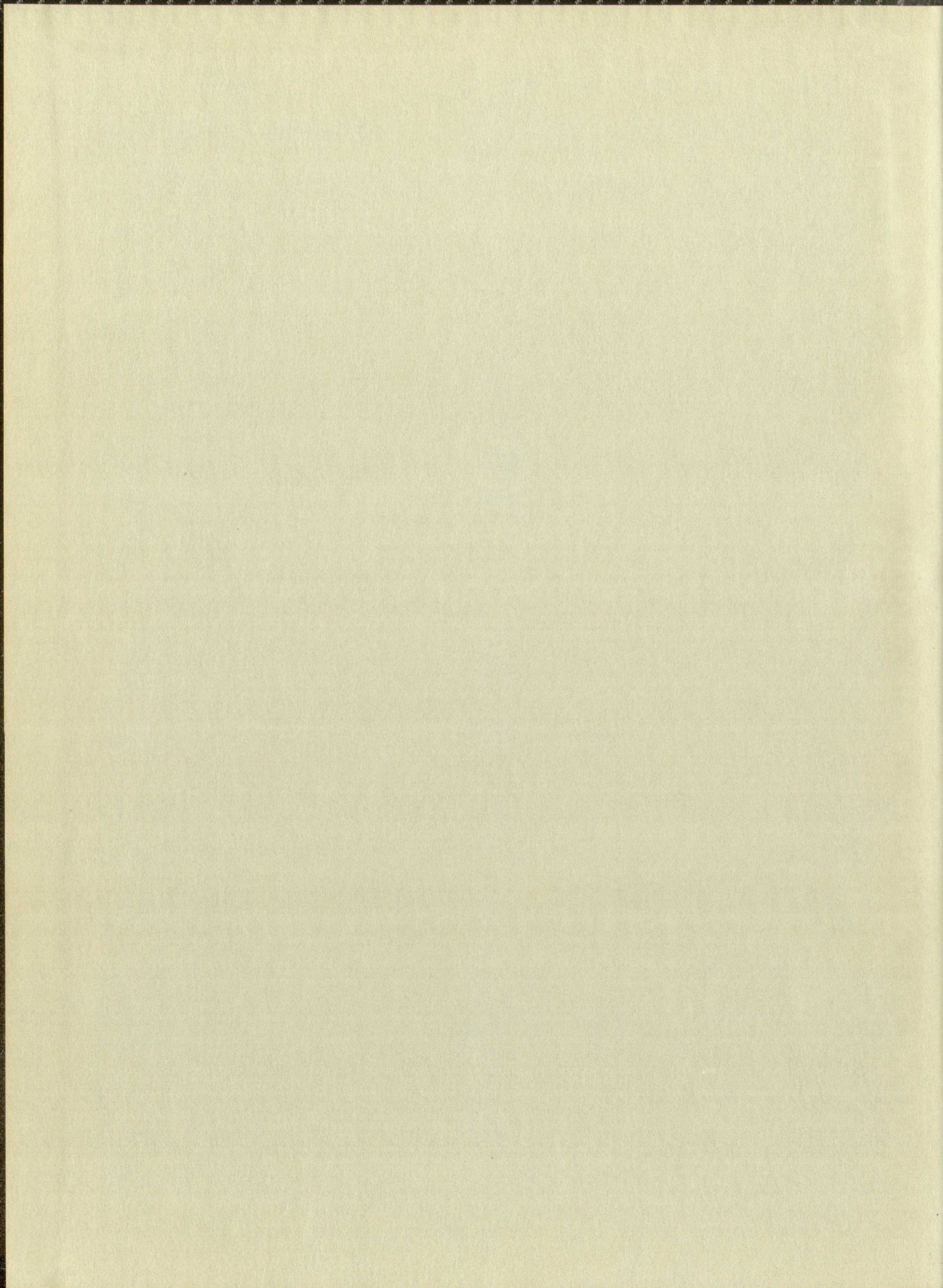
Call No.

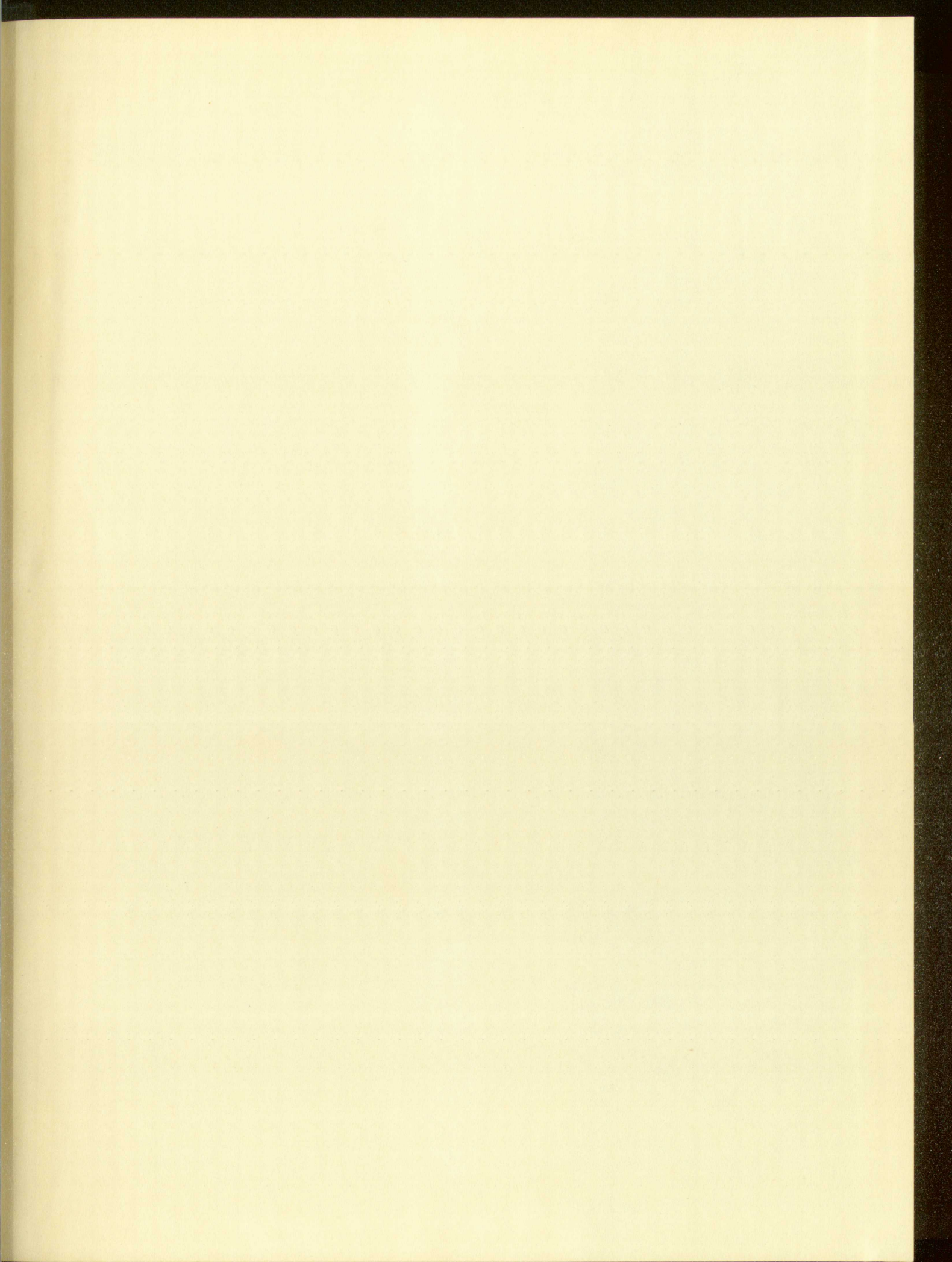
378.789
Un30fi
1959
cop.2

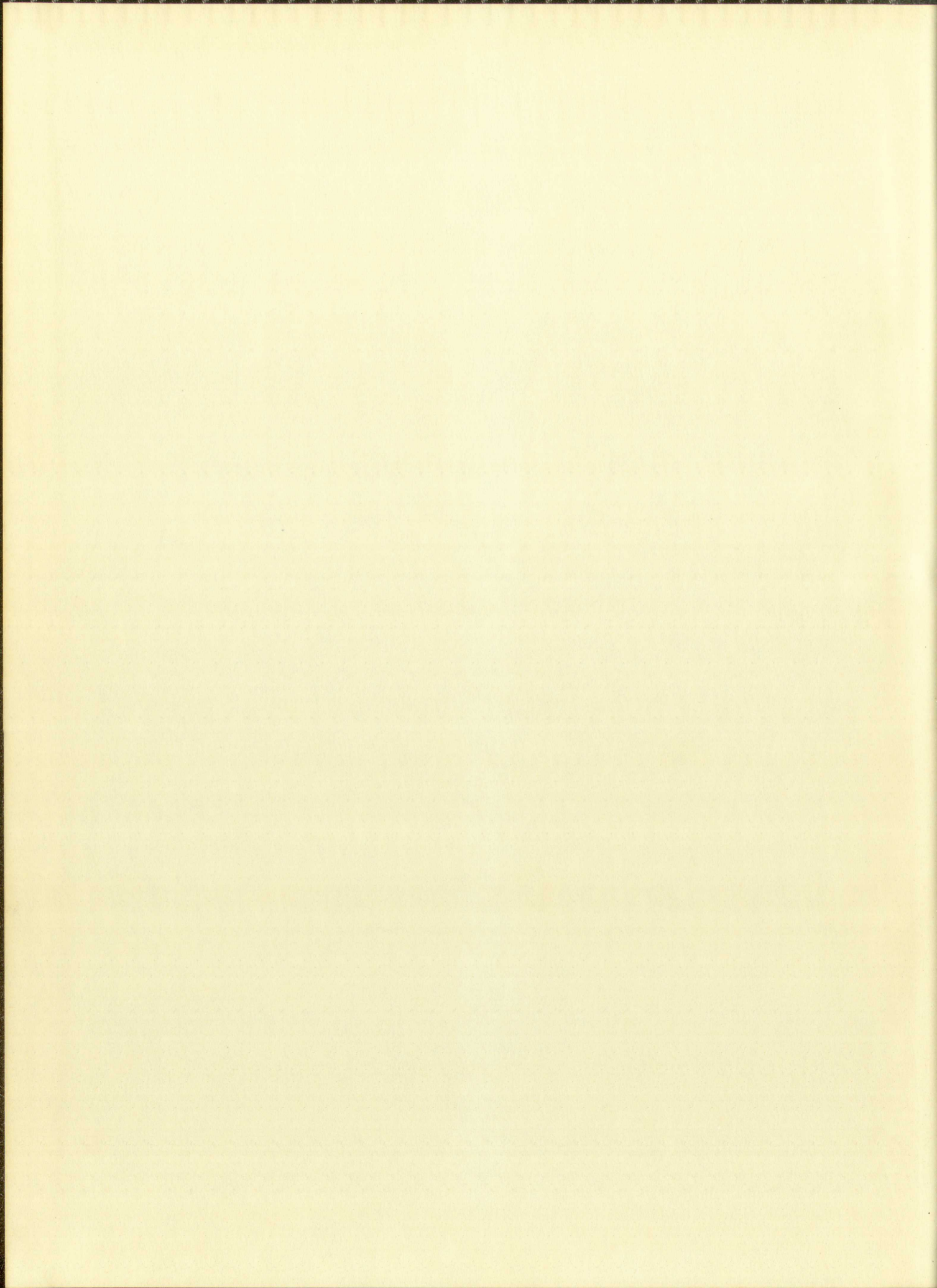
Accession
Number

247473









UNIVERSITY OF NEW BRUNSWICK LIBRARY

ACQUISITION SLIP

Unpublished documents deposited by the author in the library of
any department of the University of New Brunswick are hereby
open for inspection by the library and may be used for the purpose
of the author's biography or other historical or literary work.
The library will be pleased to accept of any such documents and
proper credit will be given in the University Catalogue for the
work. However, it is requested that the donor be made aware that
particular care should be taken to ensure that the documents are
of the University of New Brunswick.

This thesis by _____
has been used by the following persons: _____
acceptance of the donor is hereby acknowledged.

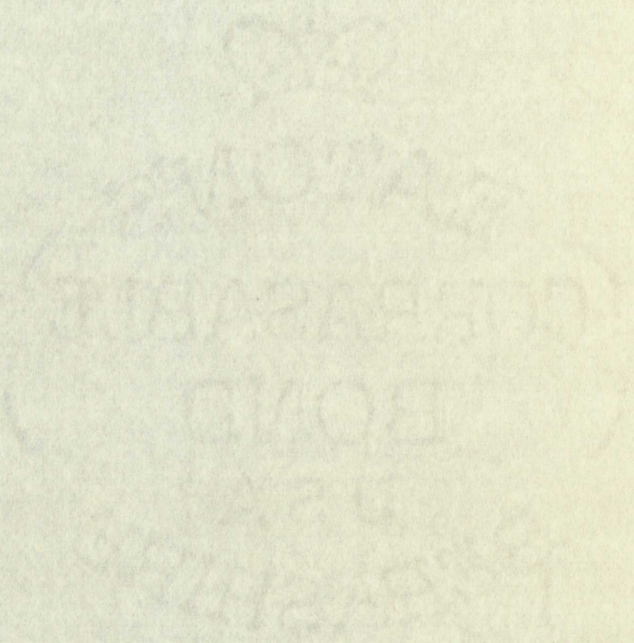
A Library stock card has been filed in the _____
expected to show the acquisition of this slip.

NAME AND ADDRESS

DATE

[Faint handwritten text, possibly a signature or name]

[Faint handwritten text]



Faint rectangular stamp or text at the bottom center of the page, possibly containing the name of a company or institution.

UNIVERSITY OF NEW MEXICO LIBRARY

MANUSCRIPT THESES

Unpublished theses submitted for the Master's and Doctor's degrees and deposited in the University of New Mexico Library are open for inspection, but are to be used only with due regard to the rights of the authors. Bibliographical references may be noted, but passages may be copied only with the permission of the authors, and proper credit must be given in subsequent written or published work. Extensive copying or publication of the thesis in whole or in part requires also the consent of the Dean of the Graduate School of the University of New Mexico.

This thesis by Joseph J. Finney.....
has been used by the following persons, whose signatures attest their acceptance of the above restrictions.

A Library which borrows this thesis for use by its patrons is expected to secure the signature of each user.

NAME AND ADDRESS

DATE

MANUSCRIPT LIBRARY

Unpublished theses submitted for the degrees and Doctors of
arts and deposited in the University of New Mexico Library are
open for inspection but are to be used only with the consent of the
rights of the authors. Bibliographical references may be made, but
passages may be copied only with the permission of the author, and
proper credit must be given in subsequent articles or published
work. Extensive copying or publication of the thesis in whole or in
part requires also the consent of the Dean of the Graduate School
of the University of New Mexico.

This thesis by _____
has been used by the following persons, whose signatures and dates
acceptance of the above restrictions

A library which borrows this thesis for use by its patrons is
expected to secure the signature of each user.

DATE

NAME AND ADDRESS

The name of the
author has been
checked and
is correct.

THE CRYSTAL STRUCTURE OF CeNi

By
Joseph J. Finney

A Thesis
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Geology

The University of New Mexico

1959



THE CRISTAL BRAND

MADE IN U.S.A.

UNBREAKABLE
BOND

Substituted in various applications
for the purpose of
making it impossible to
break the bond

The Crystal Brand

This thesis, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

St. Castetter
DEAN

May 20, 1953
DATE

Thesis committee

Abraham Rosenberg
CHAIRMAN

J. Paul Fitzsimmons

W. E. Elston

The first in a series of papers on the subject of
mineral has been published by the University of
University of Toronto, Ontario, Canada, and is
known to the public.

[Faint signature]

[Faint text]

[Faint text]

[Faint text]

[Faint text]

[Faint text]

[Faint text]

378.789
Un30fi
1959
Cop. 2

CONTENTS

	Page
Abstract.....	1
Introduction.....	2
Acknowledgments.....	2
Previous work.....	3
Experimental methods.....	8
Preparation of samples.....	8
X-ray diffraction methods.....	9
Cell constants and space group.....	12
Determination of structure.....	17
Selection of atomic positions.....	17
Structure factor.....	19
Trial parameters.....	21
Least squares refinement.....	27
Fourier synthesis.....	27
Discussion of structure.....	34
Interatomic distances.....	34
Similarity to other structure.....	34
Physical properties.....	38
Bibliography.....	39

378.787
U301
1959
Cip.2

Abstract.....

Introduction.....

Acknowledgments.....

Previous work.....

Experimental methods.....

Preparation of samples.....

X-ray diffraction.....

Cell constants and space groups.....

Determination of structure factors.....

Selection of phases.....

Structure factors.....

Final parameters.....

Least squares refinement.....

Fourier synthesis.....

Discussion of results.....

References.....

Interatomic distances.....

Summary.....

Physical properties.....

Bibliography.....

ILLUSTRATIONS

Figures

	Page
1. Phase diagram of the cerium-nickel system....	4
2. Calculated structure factors plotted against varying parameters.....	26
3. Graphic comparison of F_o and F_c for $Ok\ell$ reflections.....	29
4. Fourier projection of CeNi on (100).....	33
5. Drawing of the crystal structure of CeNi.....	36
6. Photograph of a crystal model of two cells of the CeNi structure.....	37

Tables

	Page
I. Interatomic distances for CeNi ₅ , CeNi ₂ , CeNi ₃ , Ce ₂ Ni ₇	7
II. Observed reflections of CeNi, Cu K α radiation.....	14
III. Observed reflections of CeNi, Mo K α radiation.....	15
IV. General and special positions of the space group Cmcm.....	18
V. Comparison of relative intensities with calculated structure factors for the trial parameters $y_{Ce} = .17$ and $y_{Ni} = .46$	23
VI. Observed intensities for $Ok\ell$ reflections....	24
VII. Comparison of observed intensities with calculated structure factors for various parameters for $Ok0$ reflections.....	25
VIII. Parameters of CeNi from the least squares refinement.....	28

1. Phase diagram of the system...
2. Calculated activity curves plotted against varying parameters...
3. Graphic comparison of the calculated activity curves with experimental data...
4. Further projection of the activity curves...
5. Drawing of the crystal structure...
6. Photograph of a typical specimen of the salt...

EXPERIMENTAL

- I. Introduction and description of the system...
- II. Observed activity curves...
- III. Observed activity curves...
- IV. General and special features of the phase diagram...
- V. Comparison of the calculated activity curves with experimental data...
- VI. Observed activity curves...
- VII. Comparison of observed activity curves with calculated activity curves...
- VIII. Parameters of the system...

	Page
IX. Calculated and observed structure factors for CeNi.....	30
X. Interatomic distances in CeNi.....	35

IX. Calculated and observed
for C.M.I.

X. Interference diagrams
.....

THE CRYSTAL STRUCTURE OF CeNi

ABSTRACT

X-ray diffraction methods were used to determine the cell constants and structure of CeNi. The unit cell is orthorhombic. The space group is probably Cmcn with $a_0 = 3.77 \pm 0.01$, $b_0 = 10.46 \pm 0.02$, $c_0 = 4.37 \pm 0.01$ Å. The cell formula is Ce_4Ni_4 . The observed density is 7.51 grams/cm³ and the calculated density is 7.65 grams/cm³, a deviation of 1.8%.

The trial parameters, $y_{Ce} = .14$ and $y_{Ni} = .42$, were refined by the least squares method. A Fourier synthesis gives close agreement. The structure consists of atoms of cerium and nickel in the four-fold positions, $0, y, \frac{1}{4}$; $0, \bar{y}, \frac{1}{4}$; $(+ 0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0)$; $y_{Ce} = .139 \pm .002$, $y_{Ni} = .428 \pm .004$. The minimum interatomic distances are 3.64 Å for Ce-Ce, 2.66 Å for Ni-Ni, and 2.91 Å for Ce-Ni.

The structure is similar to that of thallos iodide. Two cleavage directions are present, (010) perfect and (100) good.

THE CRYSTAL STRUCTURE OF ...

...

X-ray diffraction measurements were made on the ...

cell constants and ...

orthorhombic. The ...

$a_0 = 8.77 \pm 0.01$, $b_0 = 12.4 \pm 0.1$, $c_0 = 12.4 \pm 0.1$

The cell formula is ...

$Z = 2$ and the ...

a deviation of 1.8%

The trial parameters ...

refined by the least squares method ...

gives close agreement ...

carbon and nickel ...

$(+0.0, 0; N, 0; 0; 0; 0; 0)$

The minimum interatomic distance ...

2.35 Å for Ni-Ni ...

The structure is ...

Two cleavage directions ...

...

INTRODUCTION

The elements of the lanthanide group of rare earths are similar in size and behavior to the elements of the actinide group. In particular, cerium behaves much like plutonium in crystal structures though it is somewhat larger. A program of investigation of cerium compounds has been undertaken at the Los Alamos Scientific Laboratory because of these similarities. The present investigation is an outgrowth of that program.

The compound CeNi is one of a series of intermetallic compounds which form in the system cerium-nickel. These compounds do not occur in nature but have been produced artificially.

ACKNOWLEDGMENTS

The author wishes to thank R. E. Tate of the Los Alamos Scientific Laboratory who prepared the samples used in this study. The least squares refinement was computed by Don T. Cromer and the Fourier synthesis was computed by Allen C. Larson both of the Los Alamos Scientific Laboratory.

The United States Geological Survey allowed the use of a desk calculator which aided greatly in all computations.

The elements of the structure of the
are similar in size and shape to
atomic groups. In particular, the
structure in crystal structure is
larger. A picture of the structure
has been published in the literature
because of these similarities. The
is an outgrowth of that picture.
The compound GdCl₃ is a member of the
compounds which form in the series
compounds do not occur in nature
artificially.

The author wishes to thank
Alison Scientific Laboratory
used in this study. The data
computed by Ben T. Grover and
computed by Allan G. Larson
Scientific Laboratory.

The United States Government
of a beam calculator which
tions.

Assistance was readily given to the author by Don T. Cromer, Los Alamos Scientific Laboratory, and Abraham Rosenzweig, Assistant Professor, University of New Mexico.

The problem was released for publication by the Los Alamos Scientific Laboratory.

PREVIOUS WORK

The phase relations of the cerium-nickel system were studied by Vogel (1947) though the structures of some cerium-nickel compounds had been previously determined by Nowotny (1942). Vogel reported the four compounds Ce_3Ni , $CeNi$, $CeNi_2$ and $CeNi_5$. Two additional compounds were reported as having the probable composition $CeNi_3$ and $CeNi_4$. The existence of $CeNi_3$ was confirmed by Cromer and Olsen (1959), but no compound with the composition $CeNi_4$ was found. The compound Ce_2Ni_7 was found by Cromer and Larson (1959) and probably corresponds to that which Vogel thought to be $CeNi_4$. Compositions and melting points of the six compounds are shown in the phase diagram (Figure 1).

The crystal structures of $CeNi_2$ and $CeNi_5$ were determined by Nowotny (1942). $CeNi_2$ is cubic with the probable space group $Fd\bar{3}m$, $a_0 = 7.178 \text{ \AA}$, and cell contents Ce_8Ni_{16} . $CeNi_5$ is hexagonal with space group $P6/mmm$, $a_0 = 4.864$, $c_0 = 3.996 \text{ \AA}$, with one formula weight per cell.

... ..
Don T. Croner, Los Angeles
Alfreda Boscovitch,
New Mexico.

The problem was
the Alamos School

The phase relations of the
studied by Vogel (1937)
oxim-nickel
Keworty (1932), Vogel
Cell₁, Cell₂ and Cell₃
reported as having
Cell₄. The
and Olsen (1937)
Cell₄ was found. The
and ... (1937)
Vogel thought to be Cell₁
points of the
area (Figure 1).

The
... ..
... ..
Cell₁ is hexagonal
... ..

... ..
... ..

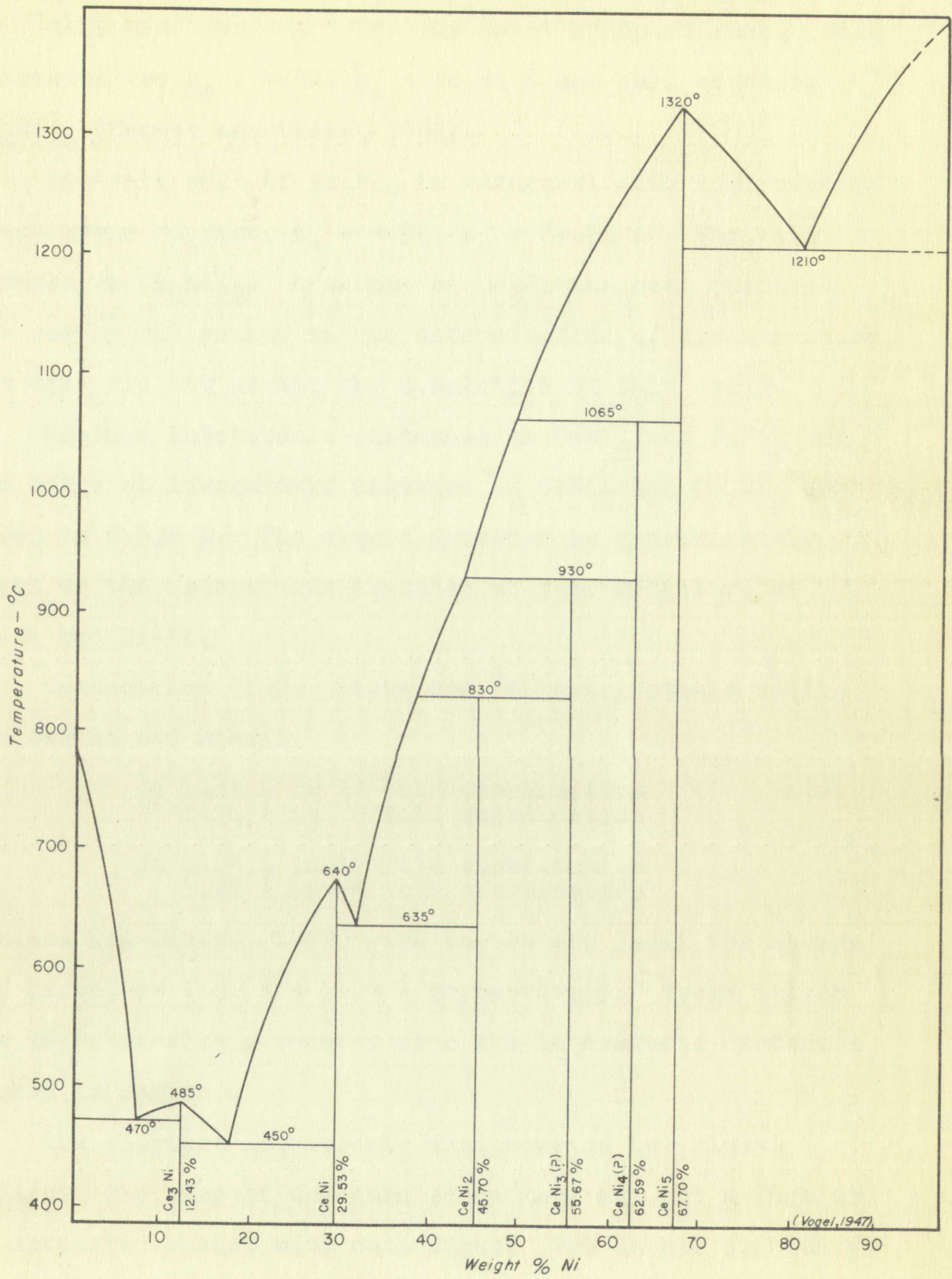


FIGURE. I - PHASE DIAGRAM OF THE CERIUM - NICKEL SYSTEM

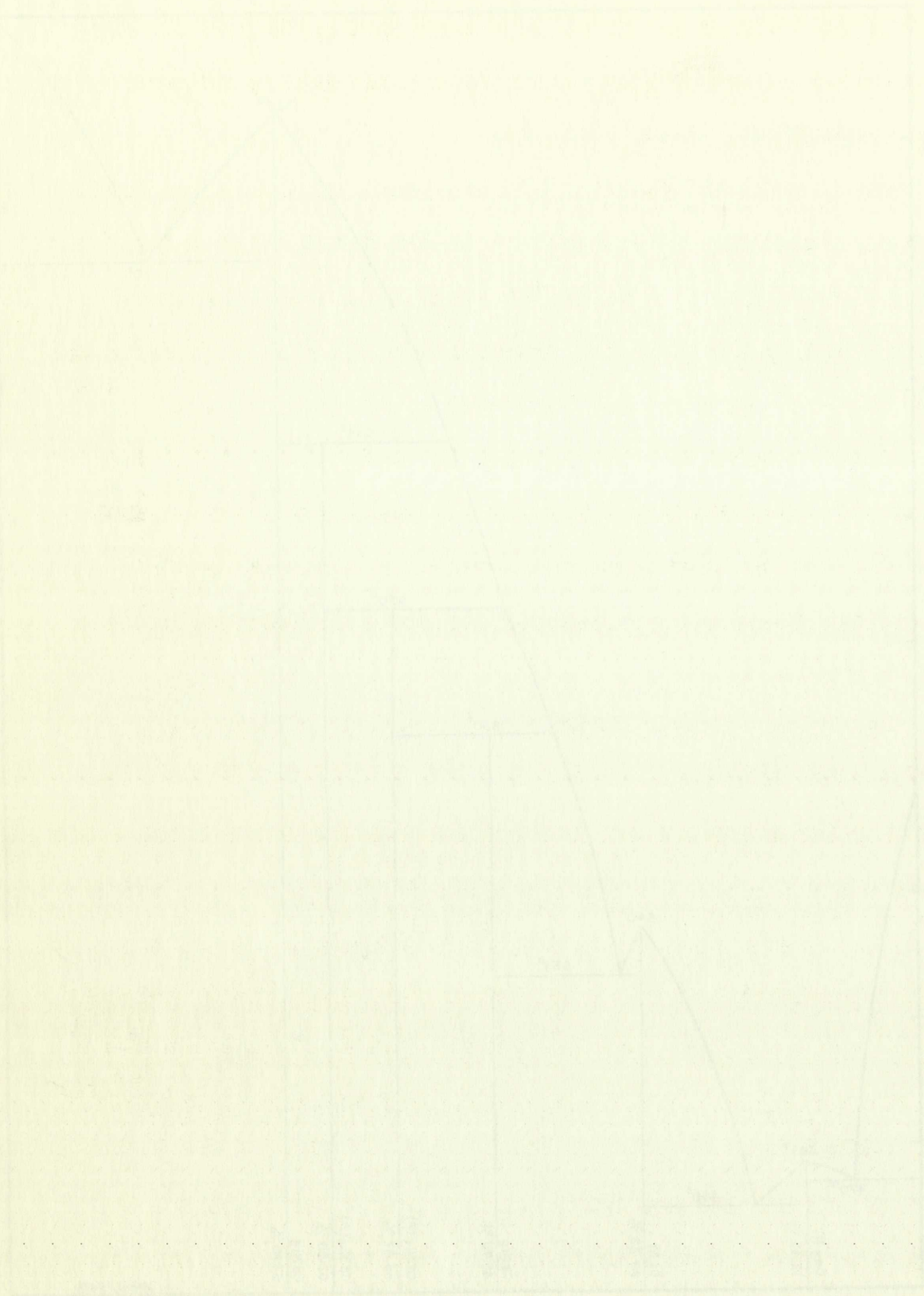


FIGURE 1. PHASE DIAGRAM OF THE CERIUM-NICKEL SYSTEM

CeNi_3 is hexagonal with the space group $P6_3/mmc$. Cell constants are $a_0 = 4.98$, $c_0 = 16.54 \text{ \AA}$ and cell contents $\text{Ce}_6\text{Ni}_{18}$ (Cromer and Olsen, 1959).

The unit cell of Ce_2Ni_7 is hexagonal with the probable space group $P6_3/mmc$, $a_0 = 4.98$, $c_0 = 24.52 \text{ \AA}$. The cell formula is $\text{Ce}_8\text{Ni}_{28}$. A sample of Ce_3Ni has been prepared for use by the author in the determination of its structure but time did not permit the completion of this study.

Minimum interatomic distances in CeNi_5 and CeNi_2 and the range of interatomic distance in CeNi_3 and Ce_2Ni_7 are shown in Table I. The atomic diameter is approximately equal to the interatomic distance of near neighbors of Ce-Ce and Ni-Ni.

Goldschmidt (1929) lists the following atomic radii for cerium and nickel:

Ce	1.81 \AA	in 12 fold coordination
	1.76 \AA	in 8 fold coordination
Ni	1.24 \AA	in 12 fold coordination
	1.21 \AA	in 8 fold coordination

Rankama and Sahama (1952) give the atomic radii for cerium and nickel as 1.82 and 1.24 \AA respectively. These values are in reasonable agreement with the interatomic distances listed in Table I.

The shortest interatomic distances do not always indicate the size of the atom since they may not always be in intimate contact with each other. The denser structures

Cells as described in the preceding section.

constants are $\epsilon = 1.0$, $\mu = 1.0$, $\rho = 1.0$, $\sigma = 1.0$.

ϵ_0 is (Gaussian and CGS) $4\pi \times 10^{-9}$.

The unit cell of CaF_2 is body centered cubic.

space group $Fm\bar{3}m$, $a = b = c = 0.356$ nm.

formula is CaF_2 .

for use of the vector in the structure factor calculation

but time did not permit the derivation of the structure factor.

Minimum refractive index is 1.48 at $\lambda = 0.5$ nm.

the range of refractive indices is 1.48 to 1.52.

shown in Table I. The refractive index is 1.52 at $\lambda = 0.4$ nm.

equal to the refractive index of CaF_2 .

Ca-Ca and Ca-F bond lengths are 0.295 nm and 0.235 nm.

for comparison purposes.

Table I. Refractive index of CaF_2 as a function of wavelength.

Wavelength (nm) Refractive index

0.4 1.52

0.5 1.48

0.6 1.46

0.8 1.44

1.0 1.43

in units of nm^{-1} .

tend to show less than average distances, while greater than average distances may appear in structures of lower densities.

The structures of CeNi and Ce₃Ni have not been previously determined.

...to show less than average ...
...than average distances ...
...referred.

The ... of ... and ...
...only ...

1950

Table I

Interatomic distances for CeNi_5 , CeNi_2 , CeNi_3 , Ce_2Ni_7

	Ce-Ce	Ce-Ni	Ni-Ni
CeNi_5	4.00 Å	2.81	2.43
CeNi_2	3.11	2.97	2.54
CeNi_3	3.19-3.44	2.86-3.22	2.49-2.88
Ce_2Ni_7	3.23-3.69	2.88-3.32	2.46-2.88

STATE OF CALIFORNIA
CORRECTIONS

Interstate Assignments

INMATE NO.	DATE	TO	FROM
12345	1-15-55	San Quentin	San Quentin
67890	2-10-55	Folsom	Folsom
11223	3-05-55	San Francisco	San Francisco
44556	4-20-55	San Francisco	San Francisco

EXPERIMENTAL METHODS

Preparation of Samples

Two samples of CeNi and one sample of Ce₃Ni were prepared by R. E. Tate by melting cerium and nickel in stoichiometric proportions in vacuum in an induction furnace. The melt was cooled slowly by gradual lowering of the furnace temperature. A portion of one sample of CeNi was annealed by heating it in a vacuum to a temperature of 620°C, just below the melting point, and holding this temperature for about two and one-half days before cooling. This was done in an attempt to produce better crystals after it was found that good single crystals could not be isolated from the unannealed material. The crystals of the annealed portion showed no improvement over the original sample.

All samples were prepared in a vacuum to avoid oxidation, since pure cerium oxidizes rapidly. The sample of Ce₃Ni oxidized and disintegrated to a black powder in a period of several weeks while at room temperature. No problem of this type was encountered with the samples of CeNi, due primarily to its lower cerium content. The samples tarnished somewhat, but this was only a surface effect.

EXPERIMENTAL

Preparation of samples

The samples of CaF_2 were prepared by R. B. ... of the furnace temperature ... CaF_2 was annealed ... of 520°C this temperature for ... cooling. ... oxysalts after it ... could not be isolated ... oxysalts of the ... over the original sample.

All samples were prepared ... oxidation, since ... sample of CaF_2 ... powder in a period ... particles. No ... the samples of CaF_2 content. The ... only a surface effect.

X-ray Diffraction Methods

Selection of a suitable wave-length of radiation for use with CeNi involved consideration of absorption effects of the elements involved. Since cerium is a high atomic number element, its absorption coefficient is generally high. The use of X-rays with short wave lengths minimizes but does not eliminate this effect. Such effects may be ignored however, if small crystals are used.

The optimum crystal size for use with Mo $K\alpha$ radiation, .711 Å, was found to be $2/\mu = .055$ mm and $2/\mu = .017$ mm for Cu $K\alpha$ radiation, 1.541 Å, (Buerger, 1942). Crystals of approximately .05 x .06 mm in cross-section were chosen and Mo $K\alpha$ radiation used. However, Cu $K\alpha$ radiation was used for the initial determination of cell constants and space group since this wave length produced relatively strong reflection for a given exposure and allowed crystals to be lined up more quickly. Crystal line-ups were effected by the method of Dragsdorf (1953).

For intensity measurements, a single crystal was oriented for $hk0$ Weissenberg photographs, but the reflections were badly elongated. When several crystals in this orientation gave similar results, a crystal was mounted parallel to the a axis and $Ok\ell$ photographs taken.

Three sheets of film were inserted into the camera in order to create a scale factor for the very strong reflections, and the exposure time set arbitrarily at

Selection of the...
 the with...
 of the...
 reader...
 right...
 but does not...
 ignored...
 The...
 VII...
 for...
 of...
 and...
 used...
 space...
 strong...
 to be...
 by...
 for...
 offered...
 with...
 orientation...
 parallel...
 Thus...
 in order...
 reflection...

sixty hours. The sixty-hour exposure time proved to be too short and another photograph was taken with the exposure set at two hundred and forty hours. This exposure yielded reflections of measurable intensity.

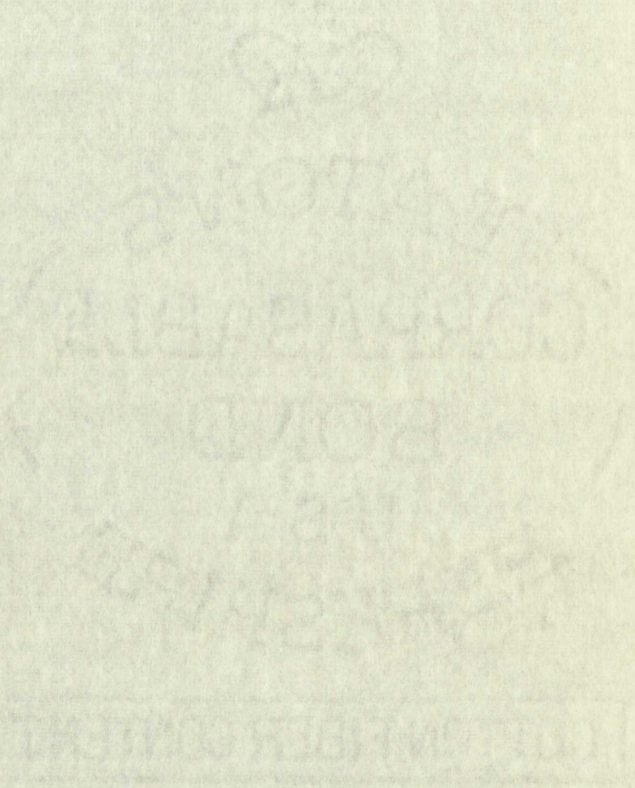
The intensities of observed reflections were evaluated by comparison with a scale of intensities of known value. A suitable strong spot was used to create this scale. The θ angle and translation distance from a known position were measured. All other reflections were blocked off and the crystal was oscillated over a narrow range. The number of oscillations was increased by 15% for each translation of the film, with the maximum number of oscillations for the set calculated to be 15% greater than the estimated intensity of this reflection on existing films. The Ok_l photograph was indexed and the intensities compared visually with the scale. Intensities were assigned values based upon the calculated number of oscillations in any one position of the film.

Because crystals are finite in size and X-ray reflection occurs over a small range of angle, reciprocal lattice points have a finite size and take time to pass through the sphere of reflection. The Lorentz factor, $(1/\sin^2\theta)$, is a measure of this time. The diffracted X-ray beam is also partially polarized. The expression $(1+\cos^2 2\theta)$ allows for this partial polarization. The combined correction for

... sixty inches. The diameter of the pipe was ...
... two inch and a half diameter ...
... was set at two hundred and fifty ...
... yielded reflections of ...
... The intensity of ...
... by comparison with a ...
... A suitable ...
... @ ...
... measured. All ...
... crystal was ...
... oscillations ...
... the film, with ...
... set ...
... six of ...
... glass ...
... with the ...
... upon the ...
... tion of the ...
... because ...
... tion occurs ...
... points ...
... sphere of ...
... measure of ...
... partially ...
... this ...

these effects is applied to the visually estimated intensities by use of the Lorentz-polarization factor, L^*p . Values of the Lorentz-polarization factor were obtained from Buerger (1941).

These effects are reported in Table 1. The values of the parameters are given in Table 2. The values of the parameters are given in Table 2. The values of the parameters are given in Table 2.



CELL CONSTANTS AND SPACE GROUP

The determination of the cell constants and space group of CeNi was accomplished by use of single crystal oscillation and Weissenberg photographs. Since nothing of the physical characteristics of CeNi was known, no information was immediately available concerning the orientation of crystals.

Oscillation and zero-level Weissenberg photographs were taken of a crystal oriented parallel to two conspicuous cleavages. Layer line spacings were measured on the oscillation photograph. Two perpendicular zone axes were found on the zero-level photograph. The crystal was then oriented perpendicular to one cleavage and parallel to the second and oscillation and zero-level photographs were taken. The layer line spacing on the oscillation photograph was the same as one of the two zone axes found on the zero-level photograph of the previous orientation. The third zone axis was present on both photographs, and in both cases was perpendicular to the other. Moreover, reflections on either side of all three zone axes were observed to be symmetrically disposed with those axes, indicating planes of symmetry.

The spacings obtained from the three zone axes were as follows:

$$\begin{aligned}a_0 &= 3.77 \text{ \AA} \pm .01 \\b_0 &= 10.46 \text{ \AA} \pm .02 \\c_0 &= 4.37 \text{ \AA} \pm .01.\end{aligned}$$

The determination of the lattice parameters of the group of C_{2h} was accomplished by means of the oscillation and layer-line methods. The physical characteristics of the oscillation were investigated by means of the oscillation of crystals.

Oscillation and layer-line methods were used to determine the lattice parameters of a crystal structure. The oscillation method is based on the measurement of the intensity of the diffraction spots. The layer-line method is based on the measurement of the intensity of the layer lines.

and oscillation and layer-line methods were used to determine the lattice parameters of a crystal structure. The oscillation method is based on the measurement of the intensity of the diffraction spots. The layer-line method is based on the measurement of the intensity of the layer lines.

The results of the oscillation and layer-line methods are given in Table 1. The lattice parameters are given in Å. The space group is C_{2h} .

TABLE 1

Since the three axes were mutually perpendicular and unequal, orthorhombic symmetry was indicated.

The above orientation of axes departs from the convention $c < a < b$, but it places the space group in a C centered orientation, which is the standard orientation, (International Tables for X-ray Crystallography, 1952).

Weissenberg photographs were taken of the levels $0k\ell$, $1k\ell$, $2k\ell$, $hk0$, $hk1$ and $hk2$ and all reflections indexed. Tables II and III list the reflections observed using Cu $K\alpha$ and Mo $K\alpha$ respectively. Reflections of the type hkl were observed only with $h+k = 2n$. In addition, in $h0\ell$ reflections, only those where $h = 2n$, $\ell = 2n$ were observed. A summary of the observed extinctions follows:

hkl	$h+k = 2n$
$0k\ell$	$(k = 2n)$
$h0\ell$	$\ell = 2n; (h = 2n)$
$hk0$	$(h+k = 2n)$
$h00$	$(h = 2n)$
$0k0$	$(k = 2n)$
00ℓ	$(\ell = 2n)$

Space groups in the orthorhombic system that display these extinctions are $Cmc2_1$, a noncentrosymmetric space group and $Cmcm$, the centrosymmetric equivalent. There was greater likelihood of the space group being $Cmcm$ because there was no morphological evidence to substantiate the

Since the above data are not available, the
unusual, approximately spherical, and
the above discussion of the structure of the
ventilation $> 2 \times 10^4$ cm is based on the
centered orientation, also in the case of
(Interaxonal fabric) of the ventricular
relaxation program, and in the case of
the, the, and, and, and, and, and, and, and,
Tables II and III show the results of the
and no in respect to the structure of the
observed only with the use of the
tion, only those that are in the
summary of the observed structure of the

- 101
- 102
- 103
- 104
- 105
- 106
- 107
- 108
- 109
- 110

Some groups in the present study
these excitation patterns, and
Group and Group, and
greater likelihood of the
there was no significant

UNIVERSITY OF CALIFORNIA

Table II

Observed reflections of CeNi, Cu $K\alpha$.

<u>hk0</u> photograph			<u>hkl</u> photograph		
200 (s)	110 (w)		021 (s)	221 (m)	
400 (s)	130 (m)		041 (s)	241 (w)	
040 (s)	170 (s)		061 (s)	261 (vw)	
060 (vvw)	1110 (s)		081 (s)	281 (vvw)	
080 (m)	240 (w-m)		0101 (s)	2101 (m)	
0100 (m-s)	2100 (w-m)		0121 (m-s)	2121 (m-s)	
0120 (vvw)	2120 (w)		111 (m)	311 (s)	
	310 (w)		131 (w-m)	331 (m)	
	330 (m)		151 (w)	351 (w)	
	370 (m)		171 (vw)	391 (m)	
	440 (m-s)		191 (w-m)	421 (m-s)	
			1111 (w)	441 (w-m)	
			1131 (m-s)	461 (m-s)	
hk2 photograph					
	042 (s)	242 (m)			
	082 (m)	282 (w-m)			
	0102 (m)	2102 (m-s)			
	0122 (w)	132 (m)			
	202 (s)	172 (s)			
	402 (m)	1112 (s)			
		332 (m)			
		372 (m-s)			

Small letters in brackets indicate relative intensity:

- (s) strong
- (m-s) moderate to strong
- (m) moderate
- (w-m) weak to moderate
- (w) weak
- (vw) very weak
- (vvw) very very weak.

TABLE

General Information of the Project

Table of Contents

1.0	1.0	1.0
2.0	2.0	2.0
3.0	3.0	3.0
4.0	4.0	4.0
5.0	5.0	5.0
6.0	6.0	6.0
7.0	7.0	7.0
8.0	8.0	8.0
9.0	9.0	9.0
10.0	10.0	10.0
11.0	11.0	11.0
12.0	12.0	12.0
13.0	13.0	13.0
14.0	14.0	14.0
15.0	15.0	15.0
16.0	16.0	16.0
17.0	17.0	17.0
18.0	18.0	18.0
19.0	19.0	19.0
20.0	20.0	20.0
21.0	21.0	21.0
22.0	22.0	22.0
23.0	23.0	23.0
24.0	24.0	24.0
25.0	25.0	25.0
26.0	26.0	26.0
27.0	27.0	27.0
28.0	28.0	28.0
29.0	29.0	29.0
30.0	30.0	30.0
31.0	31.0	31.0
32.0	32.0	32.0
33.0	33.0	33.0
34.0	34.0	34.0
35.0	35.0	35.0
36.0	36.0	36.0
37.0	37.0	37.0
38.0	38.0	38.0
39.0	39.0	39.0
40.0	40.0	40.0
41.0	41.0	41.0
42.0	42.0	42.0
43.0	43.0	43.0
44.0	44.0	44.0
45.0	45.0	45.0
46.0	46.0	46.0
47.0	47.0	47.0
48.0	48.0	48.0
49.0	49.0	49.0
50.0	50.0	50.0

Table of Contents

1.0	1.0	1.0
2.0	2.0	2.0
3.0	3.0	3.0
4.0	4.0	4.0
5.0	5.0	5.0
6.0	6.0	6.0
7.0	7.0	7.0
8.0	8.0	8.0
9.0	9.0	9.0
10.0	10.0	10.0
11.0	11.0	11.0
12.0	12.0	12.0
13.0	13.0	13.0
14.0	14.0	14.0
15.0	15.0	15.0
16.0	16.0	16.0
17.0	17.0	17.0
18.0	18.0	18.0
19.0	19.0	19.0
20.0	20.0	20.0
21.0	21.0	21.0
22.0	22.0	22.0
23.0	23.0	23.0
24.0	24.0	24.0
25.0	25.0	25.0
26.0	26.0	26.0
27.0	27.0	27.0
28.0	28.0	28.0
29.0	29.0	29.0
30.0	30.0	30.0
31.0	31.0	31.0
32.0	32.0	32.0
33.0	33.0	33.0
34.0	34.0	34.0
35.0	35.0	35.0
36.0	36.0	36.0
37.0	37.0	37.0
38.0	38.0	38.0
39.0	39.0	39.0
40.0	40.0	40.0
41.0	41.0	41.0
42.0	42.0	42.0
43.0	43.0	43.0
44.0	44.0	44.0
45.0	45.0	45.0
46.0	46.0	46.0
47.0	47.0	47.0
48.0	48.0	48.0
49.0	49.0	49.0
50.0	50.0	50.0

Table of Contents

1.0	1.0	1.0
2.0	2.0	2.0
3.0	3.0	3.0
4.0	4.0	4.0
5.0	5.0	5.0
6.0	6.0	6.0
7.0	7.0	7.0
8.0	8.0	8.0
9.0	9.0	9.0
10.0	10.0	10.0
11.0	11.0	11.0
12.0	12.0	12.0
13.0	13.0	13.0
14.0	14.0	14.0
15.0	15.0	15.0
16.0	16.0	16.0
17.0	17.0	17.0
18.0	18.0	18.0
19.0	19.0	19.0
20.0	20.0	20.0
21.0	21.0	21.0
22.0	22.0	22.0
23.0	23.0	23.0
24.0	24.0	24.0
25.0	25.0	25.0
26.0	26.0	26.0
27.0	27.0	27.0
28.0	28.0	28.0
29.0	29.0	29.0
30.0	30.0	30.0
31.0	31.0	31.0
32.0	32.0	32.0
33.0	33.0	33.0
34.0	34.0	34.0
35.0	35.0	35.0
36.0	36.0	36.0
37.0	37.0	37.0
38.0	38.0	38.0
39.0	39.0	39.0
40.0	40.0	40.0
41.0	41.0	41.0
42.0	42.0	42.0
43.0	43.0	43.0
44.0	44.0	44.0
45.0	45.0	45.0
46.0	46.0	46.0
47.0	47.0	47.0
48.0	48.0	48.0
49.0	49.0	49.0
50.0	50.0	50.0

Table III

Observed reflections of CeNi, Mo $K\alpha$.

<u>0kℓ</u> photograph				<u>lkℓ</u> photograph			
002	(s)	0101	(m)	130	(s)	113	(m-s)
004	(m)	0121	(w)	170	(m-s)	133	(m)
006	(w)	042	(s)	1110	(w-m)	153	(w)
040	(s)	023	(m)	111	(s)	193	(vw)
080	(w)	043	(m)	131	(s)	134	(w-m)
0100	(m)	063	(m)	151	(m)	174	(m)
0140	(w)	083	(w-m)	171	(vw)	115	(vw)
021	(s)	0103	(w)	191	(w)	135	(vw)
041	(s)	044	(m)	1131	(vw)		
061	(m-s)	045	(vw)	132	(m-s)		
				172	(m)		
				1112	(w)		

2k ℓ photograph

240	(m)	242	(m-s)
2101	(vw)	282	(vw)
202	(s)	223	(w-m)
204	(w-m)	243	(w)
206	(vw)	263	(w-m)
221	(m-s)	283	(vw)
241	(m)	2103	(vw)
261	(m)	244	(w)
281	(w)		
2101	(vw)		
2121	(vw)		

LIBRARY OF THE UNIVERSITY OF TORONTO

Department of Library Studies

Library Studies

Library Studies

1. Introduction
2. History of the Library
3. The Library in Society
4. The Library as a Service
5. The Library as a Business
6. The Library as a Cultural Institution
7. The Library as a Social Institution
8. The Library as a Political Institution
9. The Library as a Religious Institution
10. The Library as a Scientific Institution

(a) 1010 (a) 500
(a) 1011 (a) 400
(a) 1012 (a) 300
(a) 1013 (a) 200
(a) 1014 (a) 100
(a) 1015 (a) 000
(a) 1016 (a) 000
(a) 1017 (a) 000
(a) 1018 (a) 000
(a) 1019 (a) 000
(a) 1020 (a) 000
(a) 1021 (a) 000
(a) 1022 (a) 000
(a) 1023 (a) 000
(a) 1024 (a) 000
(a) 1025 (a) 000

Library Studies

1. Introduction
2. History of the Library
3. The Library in Society
4. The Library as a Service
5. The Library as a Business
6. The Library as a Cultural Institution
7. The Library as a Social Institution
8. The Library as a Political Institution
9. The Library as a Religious Institution
10. The Library as a Scientific Institution

LIBRARY OF THE UNIVERSITY OF TORONTO
Department of Library Studies
100 St. George Street
Toronto, Ontario
M5S 1A5
Canada

noncentrosymmetric space group and because a trial structure using Cmc₂m atomic positions was possible.

The density of the samples of CeNi was found to be 7.51 grams/cm³, by the pycnometer method. The volume of the unit cell was calculated as 172.5 Å³. The number of molecules per cell can be calculated from the formula:

$$Z = \frac{\rho A_v V}{M}$$

where ρ = the observed density, A_v = Avogadro's number, V = volume of the unit cell and M = molecular weight of the compound, 198.82. $Z = 3.92$ and the cell formula is Ce₄Ni₄. The same formula can be rearranged to calculate the density of the compound. For this purpose $Z = 4$ and the density, ρ , is calculated as 7.65 grams/cm³, a deviation of 1.8% from the observed density.

EXPERIMENTAL

Nonstoichiometric compounds were prepared by the method of using Goussier's apparatus as described in the literature.

The density of the samples was determined by the method of 7.51 grams/cm³ by the pycnometer method. The density of the unit cell was obtained from the lattice parameters and the molecular weight of the compound.

$$\rho = \frac{ZM}{V}$$

where ρ = the density (g/cm³), Z = the number of molecules per unit cell, M = the molecular weight of the compound, V = volume of the unit cell (cm³). The same formula can be used to calculate the density of the compound if the lattice parameters and the molecular weight are known. The density of the compound is 7.51 g/cm³ and the molecular weight is 138.13 g/mol. The density of the compound is 7.51 g/cm³ and the molecular weight is 138.13 g/mol.

DETERMINATION OF STRUCTURE

Selection of Atomic Positions

The general and special positions for the space group $Cmcm$ are listed in Table IV, reproduced from International Tables for X-ray Crystallography (1952). It was at once evident that since only four atoms of each kind occupied the unit cell, none of the sixteen- or eight-fold positions could accommodate the atoms and still retain the symmetry of the group. This eliminated all but the four-fold positions (a), (b), and (c). The two sets (a) and (b) were attempted first.

In these positions two atoms occupy positions along the c axis. Two atoms of cerium placed in this position would occupy 7.28 Å. Two atoms of nickel would occupy 4.98 Å. The c axis length of 4.37 Å was clearly not long enough to accommodate either cerium or nickel atoms in these positions. Furthermore, placing the atoms in positions (a) and (b) would have introduced the extinction $hk\ell$, with $\ell = 2n$ only, and reflections violating this extinction were present.

The remaining four-fold position, (c), was that in which atoms were located at $0, y, \frac{1}{4}$; $0, \bar{y}, \frac{3}{4}$; $\frac{1}{2}, \frac{1}{2}+y, \frac{3}{4}$; $\frac{1}{2}, \frac{1}{2}-y, \frac{3}{4}$.

UNCLASSIFIED

CONFIDENTIAL

CONFIDENTIAL

The general...
Once the...
evident...
the...
could...
of the...
tions...
extended...

To...
the...
would...
4.98...
enough...
these...
tions...
The...
which...

The...
which...

Table IV

General and special positions of the space group Cmc₂m.

Coordinates of equivalent positions:

$(0,0,0; \frac{1}{2}, \frac{1}{2}, 0)^+$

- (h) 16: $x, y, z; x, \bar{y}, \bar{z}; x, y, \frac{1}{2}-z; x, \bar{y}, \frac{1}{2}+z;$
 $\bar{x}, \bar{y}, \bar{z}; \bar{x}, y, z; \bar{x}, \bar{y}, \frac{1}{2}+z; \bar{x}, y, \frac{1}{2}-z.$
- (g) 8: $x, y, \frac{1}{4}; \bar{x}, y, \frac{1}{4}; x, \bar{y}, \frac{3}{4}; \bar{x}, \bar{y}, \frac{3}{4}.$
- (f) 8: $0, y, z; 0, \bar{y}, \bar{z}; 0, y, \frac{1}{2}-z; 0, \bar{y}, \frac{1}{2}+z.$
- (e) 8: $x, 0, 0; \bar{x}, 0, 0; x, 0, \frac{1}{2}; \bar{x}, 0, \frac{1}{2}.$
- (d) 8: $\frac{1}{4}, \frac{1}{4}, 0; \frac{1}{4}, \frac{3}{4}, 0; \frac{1}{4}, \frac{1}{4}, \frac{1}{2}; \frac{1}{4}, \frac{3}{4}, \frac{1}{2}.$
- (c) 4: $0, y, \frac{1}{4}; 0, \bar{y}, \frac{3}{4}.$
- (b) 4: $0, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}.$
- (a) 4: $0, 0, 0; 0, 0, \frac{1}{2}.$

COPIED FROM
CORRESPONDENCE
OF THE
OFFICE OF THE
SECRETARY OF THE
NAVY

Table IV

General and special positions of the space group C_{2h}

Coordinates of equivalent positions:

(0, 0, 0; x, y, z)

- (a) 4: 0, 0, 0; x, y, z
- (b) 4: x, y, z; x, y, z; x, y, z; x, y, z
- (c) 4: 0, y, z; x, y, z; x, y, z; x, y, z
- (d) 4: x, y, z; x, y, z; x, y, z; x, y, z
- (e) 8: 0, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z
- (f) 8: x, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z
- (g) 8: x, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z
- (h) 8: x, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z; x, y, z

Structure Factor

The structure factor (structure amplitude) is a function of the relative positions of the atoms and their effective scattering of X-rays. The effective scattering is the atomic scattering factor f_n and the general structure amplitude is represented by the equation:

$$F_{\underline{hkl}} = \sum_{n=1}^N f_n \cdot e^{2\pi i(\underline{hx}_n + \underline{ky}_n + \underline{lz}_n)}$$

The exponential term may be expanded to the form:

$$\cos 2\pi(\underline{hx} + \underline{ky} + \underline{lz}) + i \sin 2\pi(\underline{hx} + \underline{ky} + \underline{lz}) = A + iB.$$

For the space group Gmcm, the terms A and B become:

$$A = 16 \cdot \cos^2 2\pi \frac{(\underline{h} + \underline{k})}{4} \cos 2\pi \underline{hx} \cos 2\pi(\underline{ky} + \underline{l}/4) \cos 2\pi(\underline{lz} + \underline{l}/4)$$

$$B = 0.$$

(International Tables for X-ray Crystallography, 1952).

For the condition $\underline{h} + \underline{k} = 2n$, $\underline{l} = 2n$:

$$A = 16 \cdot \cos 2\pi \underline{hx} \cos 2\pi \underline{ky} \cos 2\pi \underline{lz},$$

and for the condition $\underline{h} + \underline{k} = 2n$, $\underline{l} = 2n+1$:

$$A = -16 \cos 2\pi \underline{hx} \sin 2\pi \underline{ky} \sin 2\pi \underline{lz}.$$

These are expressions for atoms in sixteen-fold positions.

1952

1952

The structure of the... function of the... effective... is the... true...
The structure of the... function of the... effective... is the... true...
The structure of the... function of the... effective... is the... true...

$$\sum_{i=1}^n x_i = n$$

The exponential...
The exponential...

$$\cos(x-y) = \cos x \cos y + \sin x \sin y$$

For the...
For the...

$$A = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix}$$

$$B = 0$$

(International...)
(International...)

For the...
For the...

$$A = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix}$$

and for the...
and for the...

$$A = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix}$$

These are...
These are...

For atoms in the four-fold positions, for the condition $\underline{h+k} = 2n$, $\underline{l} = 2n$, the expression becomes:

$$A = 4\cos 2\pi \underline{h}x \cos 2\pi \underline{k}y \cos 2\pi \underline{l}z.$$

For the condition $\underline{h+k} = 2n$, $\underline{l} = 2n+1$, it becomes:

$$A = -4\cos 2\pi \underline{h}x \sin 2\pi \underline{k}y \sin 2\pi \underline{l}z.$$

For reflections of the type $0\underline{k}\underline{l}$, the expressions are further reduced to:

$$A = 4\cos 2\pi \underline{k}y \cos \pi \underline{l}/2, \text{ where } \underline{h+k} = 2n, \underline{l} = 2n$$

$$A = -4\sin 2\pi \underline{k}y \sin \pi \underline{l}/2, \text{ where } \underline{h+k} = 2n, \underline{l} = 2n+1,$$

since $\underline{h} = 0$ and $z = \frac{1}{4}$.

The complete structure factor expression for $0\underline{k}\underline{l}$ reflections where $\underline{h+k} = 2n$, $\underline{l} = 2n$ becomes:

$$F_{0\underline{k}\underline{l}} = 4 \left[f_{\text{Ce}} \cos 2\pi \underline{k}y_{\text{Ce}} \cos \pi \underline{l}/2 + f_{\text{Ni}} \cos 2\pi \underline{k}y_{\text{Ni}} \cos \pi \underline{l}/2 \right]$$

where $\underline{h+k} = 2n$, $\underline{l} = 2n+1$, it becomes:

$$F_{0\underline{k}\underline{l}} = -4 \left[f_{\text{Ce}} \sin 2\pi \underline{k}y_{\text{Ce}} \sin \pi \underline{l}/2 + f_{\text{Ni}} \sin 2\pi \underline{k}y_{\text{Ni}} \sin \pi \underline{l}/2 \right].$$

The atomic scattering factor for cerium, f_{Ce} , was taken from Internationale Tabellen (1935), and that for nickel, f_{Ni} , from Viervoll and Ögrim (1949).

The atoms in the FeO lattice are arranged in a regular array.

$$h+k = 2n, \quad l = 2m, \quad n, m \text{ integers}$$

A FeO unit cell is shown in the figure.

For the condition $h+k = 2n, l = 2m$, the structure factor is

$$F_{hkl} = f \sum_{j=1}^4 \exp(i\pi h x_j + i\pi k y_j + i\pi l z_j)$$

For reflections of the type h, k, l , the structure factor is

$$F_{hkl} = f [1 + (-1)^h + (-1)^k + (-1)^l]$$

A FeO unit cell is shown in the figure.

A FeO unit cell is shown in the figure.

$$\text{since } h, k, l = 0 \text{ and } 2, 2, 2$$

The complete structure factor is given by

$$F_{hkl} = f [1 + (-1)^h + (-1)^k + (-1)^l]$$

where $h, k, l = 0, 2, 2, 2$

$$F_{002} = f [1 + 1 + 1 + 1] = 4f$$

where $h, k, l = 2, 2, 2$

$$F_{222} = f [1 + (-1)^2 + (-1)^2 + (-1)^2] = 4f$$

The atomic scattering factor f is given by

taken from International Tables for Crystallography

nickel, $f = 10$

Trial Parameters

Whether both cerium and nickel atoms could be fitted into the unit cell in two sets of the four-fold position (c) could not be ascertained by inspection. Since the density of the compound was high, it seemed likely that the two atoms would be close together. Therefore, for the initial determination of the y parameter for cerium and for nickel, hereafter designated y_{Ce} and y_{Ni} , the cerium atom was placed with the center of the atom one radius in along the b axis and a distance of $\frac{1}{4}$ of the unit cell up along the c axis. The nickel atom was placed in contact with the cerium atom on the b axis and also $\frac{1}{4}$ of the unit cell up along the c axis. Such a selection of a y parameter was completely arbitrary. However, a graphical solution indicated that placement of the cerium and nickel atoms in these positions was possible, and gave $y_{\text{Ce}} = .17$ and $y_{\text{Ni}} = .46$ as a first approximation of the parameters.

With the derivation of the complete structure factor expression and a set of trial parameters, it was now possible to calculate the intensities of expected reflections. The values calculated from the parameters $y_{\text{Ce}} = .17$ and $y_{\text{Ni}} = .46$ for certain reflections are compared to relative observed intensities in Table V. The lack of agreement of the observed intensities and calculated values indicated that these parameters were not correct. The reflection 040

Initial Determination

Whether the... into the... (e) could not be... density of the... the two... initial determination... for nickel... atom was placed... along the... along the... with the... call up... meter was... section indicated... atoms in... and $Y_{Ni} = 0.40$... With the... expression... able to... The values... $Y_{Ni} = 0.40$... conserved... the observed... that these parameters...

is strong yet the calculated value indicated it should be weak. The reflection 060 is not observed but is calculated as being strong, as is the case for 0120. The reflection 080 is of moderate intensity whereas it is calculated to be strong. 0140 is present as a weak reflection yet it is calculated to be strong.

Since the original parameters were not suitable, it was decided to plot varying parameters for cerium and nickel against calculated intensities for $Ok0$ reflections, and compare the resulting set of curves with observed intensities. Figure 2 is the graphical representation of the calculated structure factors plotted against parameters varying from $y_{Ce} = .18$ and $y_{Ni} = .46$ to $y_{Ce} = .14$ and $y_{Ni} = .42$ in intervals of .01. The parameters $y_{Ce} = .14$ and $y_{Ni} = .42$ were in best agreement with the observed values.

The observed intensities for all $Ok\ell$ reflections, together with corrections for the $L \cdot p$ factor, are shown in Table VI. The observed intensity and structure factor could be compared more easily if the square root of the observed intensity was taken, since the structure factor is proportional to the square root of the intensity. However, the sign of such values could not be determined. Table VII shows the comparison $\sqrt{I_o/L \cdot p}$, with calculated structure factors for various parameters for $Ok0$ reflections only.

REPORT

is shown for the first time in this report. The results are given in Table I. The results are given in Table I. The results are given in Table I.

TABLE I
RESULTS OF THE EXPERIMENT

was observed in the first experiment. The results are given in Table I. The results are given in Table I. The results are given in Table I.

Figure 1 is a plot of the results. The results are given in Table I. The results are given in Table I. The results are given in Table I.

TABLE II
RESULTS OF THE EXPERIMENT

together with the results of the first experiment. The results are given in Table I. The results are given in Table I. The results are given in Table I.

TABLE III
RESULTS OF THE EXPERIMENT

shows the results of the experiment. The results are given in Table I. The results are given in Table I. The results are given in Table I.

Table V

Comparison of relative intensities (I_{rel}), with calculated structure factors (F_c) for the trial parameters $y_{Ce} = .17$, $y_{Ni} = .46$.

Index	I_{rel}^*	F_c
040	s	-6.17
060	o	+40.81
080	m	-28.81
0100	m	-17.43
0120	o	+14.00
0140	m	-23.60

* s=strong; m=moderate; o=absent.

CONFIDENTIAL

CONFIDENTIAL

Department of Defense
with related activities and
the total operations of the

Index	
0-0	
0-20	
0-30	
0-40	
0-50	
0-60	
0-70	
0-80	
0-90	
0-100	

CONFIDENTIAL

Table VI

Observed intensities for $Ok\ell$ reflections

k	ℓ	I_0	$L \cdot p$	$I_0/L \cdot p$	$\sqrt{I_0/L \cdot p}$
0	2	7030	5.93	1192.0	34.50
0	4	358	2.63	136.0	11.70
0	6	74	1.50	49.3	7.02
2	0	0	-	-	-
4	0	2405	7.17	335.0	18.30
6	0	0	-	-	-
8	0	90	3.28	27.4	5.23
10	0	105	2.50	42.0	6.48
12	0	0	-	-	-
14	0	74	1.54	49.3	7.02
2	1	2250	9.20	244.6	15.64
4	1	1170	6.09	238.1	15.43
6	1	690	4.25	162.4	12.75
8	1	194	3.12	62.2	7.91
10	1	128	2.40	61.3	7.83
12	1	64	1.55	41.3	6.43
2	2	64	5.41	11.8	3.41
4	2	1120	4.40	254.5	15.95
6	2	0	-	-	-
8	2	85	2.72	31.3	5.59
10	2	74	2.16	34.3	5.86
2	3	185	3.58	51.7	7.19
4	3	224	3.14	71.3	8.44
6	3	180	2.70	66.7	8.17
8	3	100	2.27	44.1	6.64
10	3	85	1.91	44.5	6.67
2	4	0	-	-	-
4	4	150	2.38	63.0	7.94
6	4	0	-	-	-
8	4	0	-	-	-
10	4	0	-	-	-
2	5	0	-	-	-
4	5	74	1.81	40.9	6.40
6	5	0	-	-	-
8	5	0	-	-	-
2	6	0	-	-	-

Table VII

Comparison of observed intensities, $\sqrt{I_o/L \cdot p}$, with calculated structure factors, F_c , for various parameters for $Ok0$ reflections.

Index	$\sqrt{I_o/L \cdot p}$	F_c	F_c	F_c	F_c	F_c
		$y_{Ce} = .14$.15	.16	.17	.18
		$y_{Ni} = .42$.43	.44	.45	.46
040	18	-52	-42	-28	-13	+3
060	absent	+3	+15	+27	+33	+36
080	5	+15	-4	-22	-34	-38
0100	6	-20	-34	-35	-22	-1
0120	absent	-1	+14	+21	+17	+3
0140	7	+31	+29	-4	-21	-33

COMMUNICATIONS SECTION
U.S. AIR FORCE
OFFICE OF THE SECRETARY
WASHINGTON, D.C.

1. [Illegible]	040
2. [Illegible]	050
3. [Illegible]	060
4. [Illegible]	070
5. [Illegible]	080
6. [Illegible]	090
7. [Illegible]	100

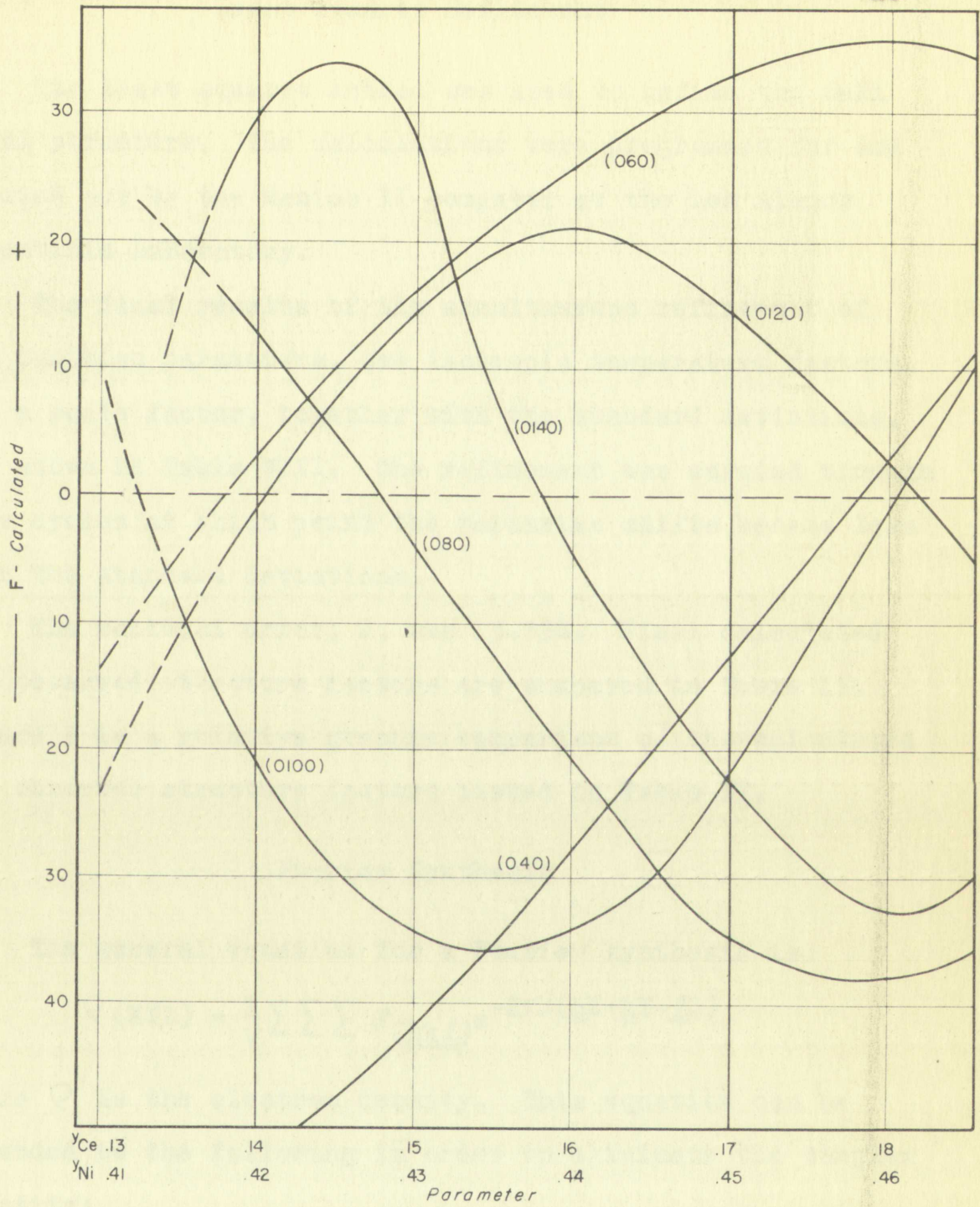


FIGURE. 2 — CALCULATED STRUCTURE FACTORS PLOTTED AGAINST VARYING PARAMETERS.

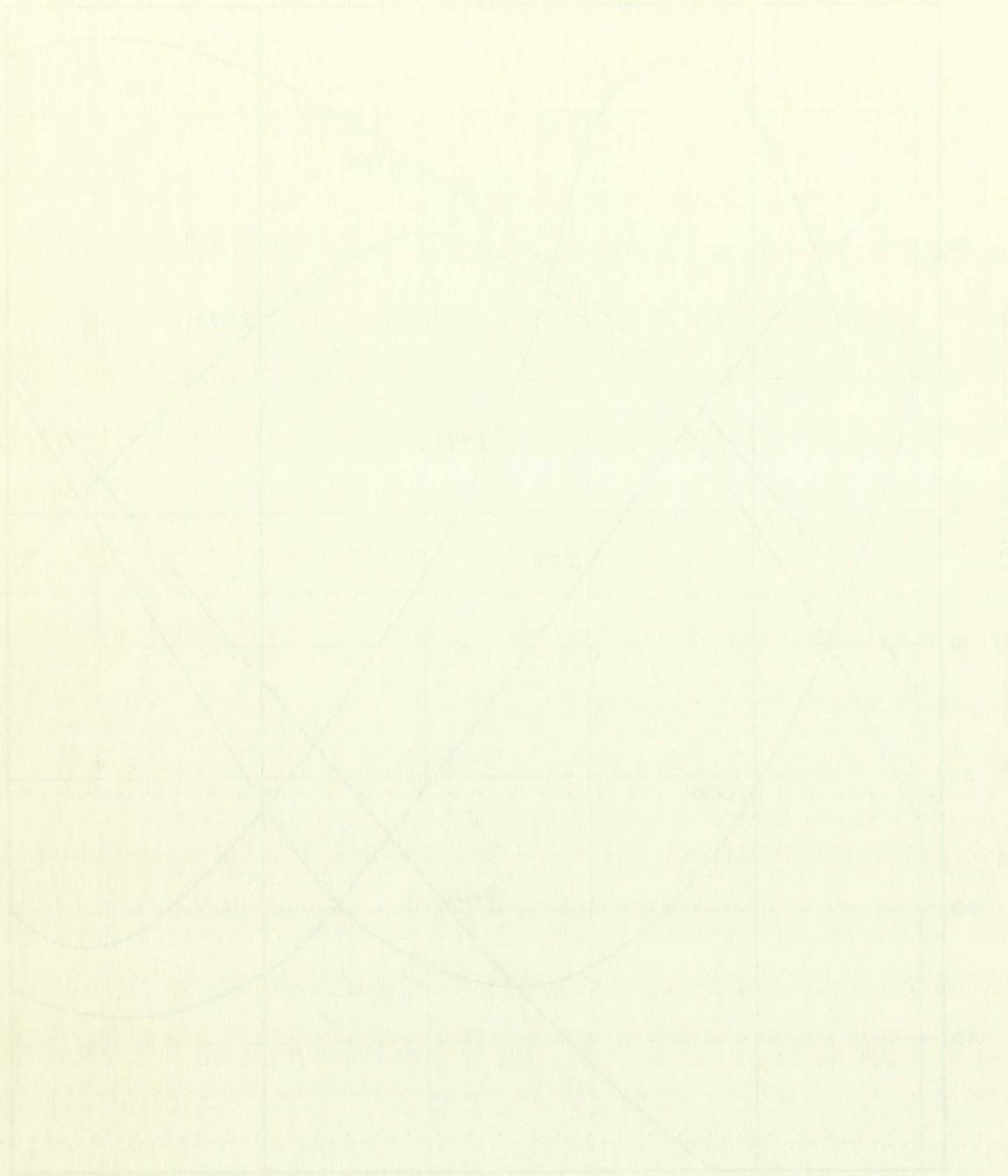


FIGURE 2 - CALCULATED STRUCTURE FACTORS PLOTTED AGAINST VARIOUS PARAMETERS

Least Squares Refinement

The least squares method was used to refine the CeNi trial structure. The calculations were programmed for and carried out by the Maniac II computer at the Los Alamos Scientific Laboratory.

The final results of the simultaneous refinement of two position parameters, two isotropic temperature factors, and a scale factor, together with the standard deviations, are shown in Table VIII. The refinement was carried through five cycles at which point the parameter shifts became less than the standard deviations.

The residual error, R, was 15.85%. Final calculated and observed structure factors are compared in Table IX. Figure 3 is a relative graphic comparison of the calculated and observed structure factors listed in Table IX.

Fourier Synthesis

The general equation for a Fourier synthesis is:

$$\rho(\underline{XYZ}) = \frac{1}{V} \sum \sum \sum F(\underline{hkl}) e^{-2\pi i(\underline{hX} + \underline{kY} + \underline{lZ})}$$

where ρ is the electron density. This equation can be expanded to the following in order to eliminate the complex quantity:

$$\rho(\underline{XYZ}) = \frac{1}{V} \left[F(000) + 2 \sum \sum \sum A(\underline{hkl}) \cos 2\pi(\underline{hX} + \underline{kY} + \underline{lZ}) + \sum \sum \sum B(\underline{hkl}) \sin 2\pi(\underline{hX} + \underline{kY} + \underline{lZ}) \right]$$

608

The first experiment was carried out at the University of Cambridge. The object was to determine the relative positions of the two principal axes of the crystal and a series of measurements were shown in Figure 1. The five cycles of the experiment were carried out in the following order:

The residual stress was observed after the crystal had been subjected to a series of stresses and the results are shown in Figure 2. Figure 3 is a relative stress diagram and observed stress diagram.

The general expression for the stress is given by

$$\sigma = \frac{1}{2}(\sigma_1 + \sigma_2) + \frac{1}{2}(\sigma_1 - \sigma_2)\cos 2\theta$$

where θ is the angle between the stress direction and the direction of the principal stress.

quantity

$$\sigma = \frac{1}{2}(\sigma_1 + \sigma_2) + \frac{1}{2}(\sigma_1 - \sigma_2)\cos 2\theta$$

Table VIII

Parameters of CeNi from the least squares refinement

Atom	y_n	$B \times 10^{16} \text{ cm}^2$
Ce	$.1394 \pm .0018$	$2.27 \pm .49$
Ni	$.4277 \pm .004$	3.08 ± 1.14

1957
DIVISION
OF INVESTIGATION
FEDERAL BUREAU OF
INVESTIGATION
U. S. DEPARTMENT OF JUSTICE

MEMORANDUM FOR THE DIRECTOR
FROM: SAC, [illegible]
SUBJECT: [illegible]

CONFIDENTIAL

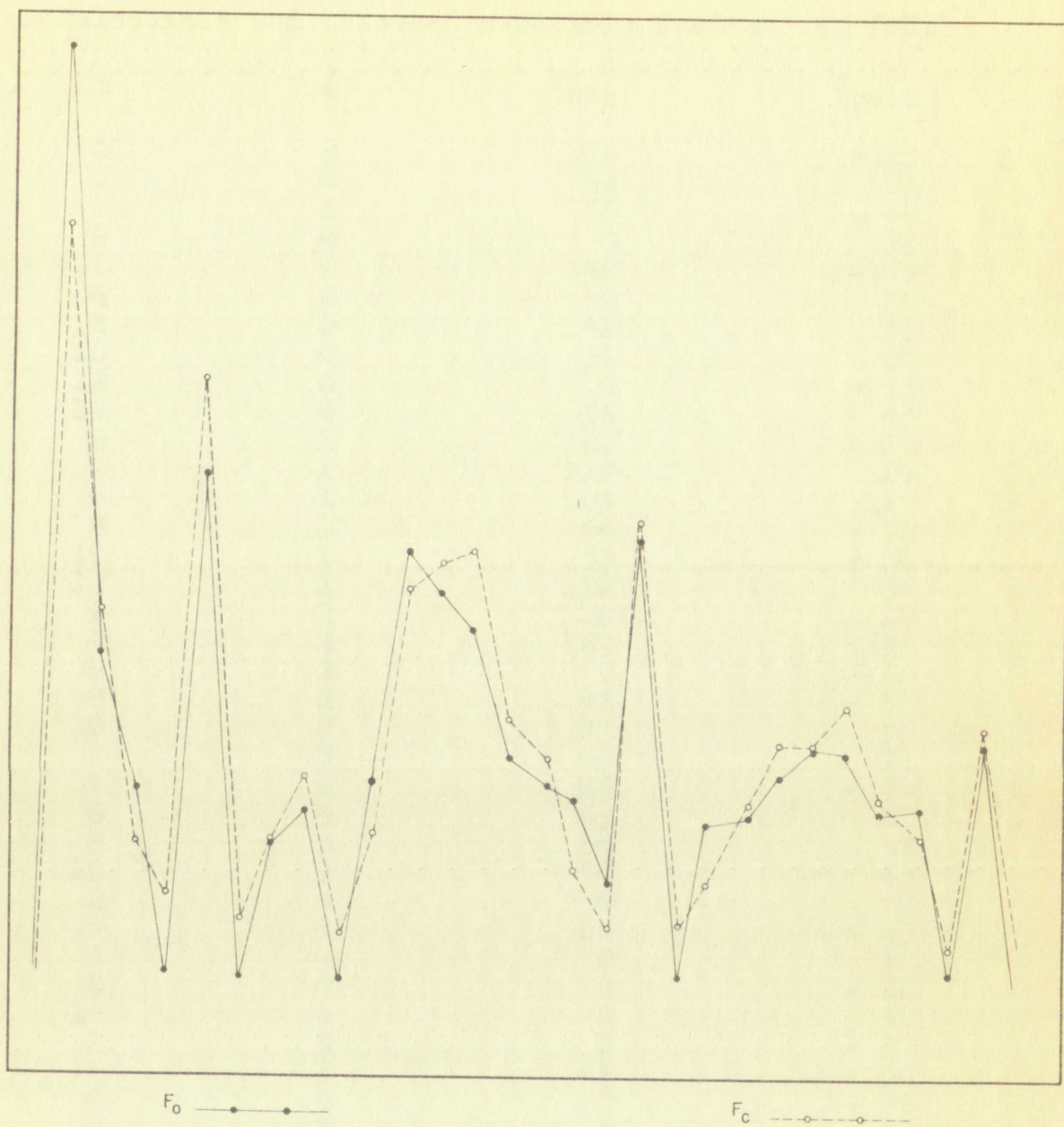
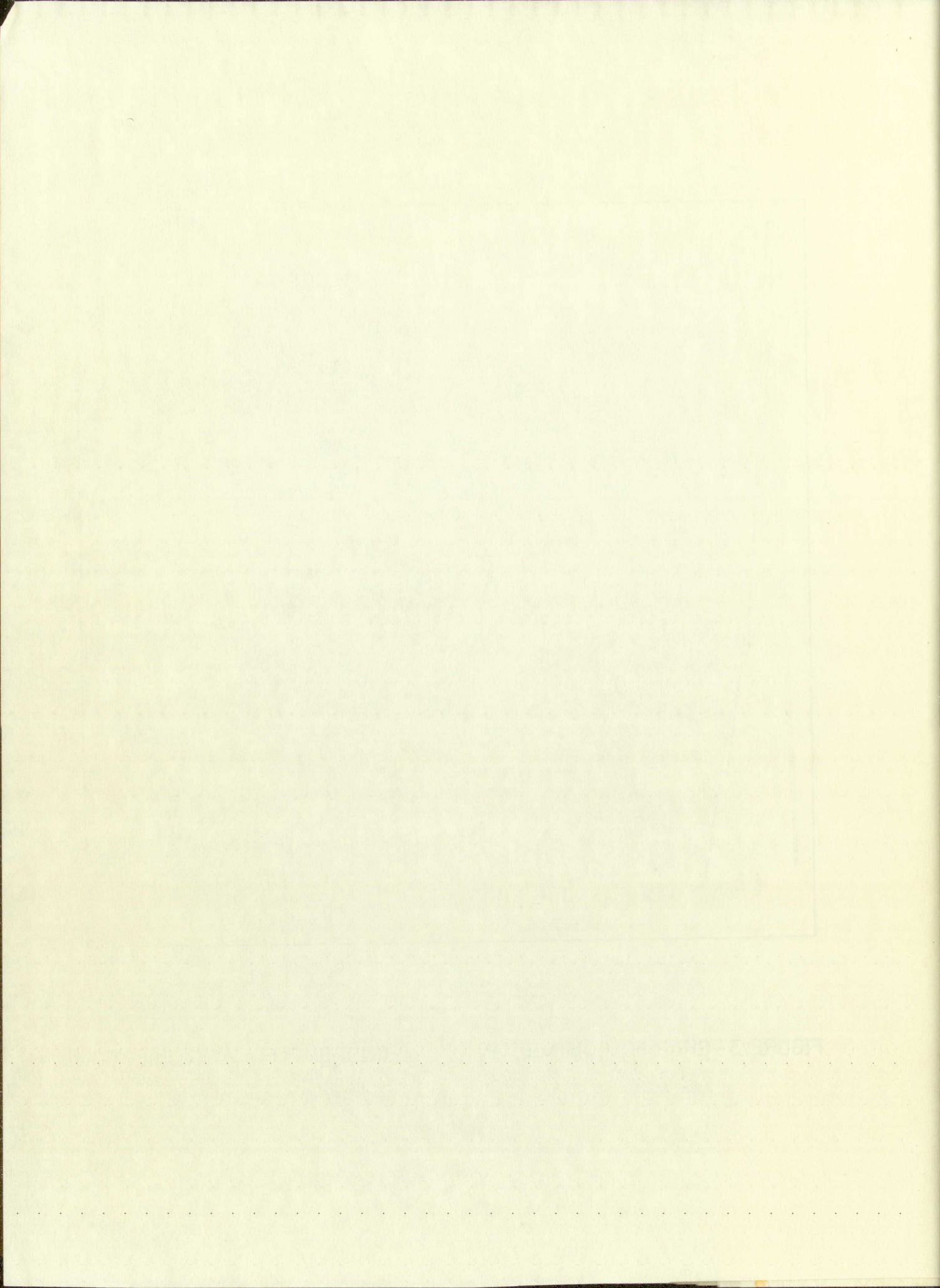


FIGURE.3- GRAPHIC COMPARISON OF F_0 AND F_c FOR $Ok\ell$ REFLECTIONS.

Table IX values of F_0 and F_c read from top to bottom are plotted from left to right.



The equation may be read: Table IX

Calculated and observed structure factors for CeNi

k	l	F_{obs}	F_{calc}
0	2	273	-223
0	4	94	105
0	6	53	-42
2	0	0	23
4	0	148	-177
6	0	0	16
8	0	41	39
10	0	51	60
12	0	0	-13
14	0	56	43
2	1	127	-115
4	1	112	124
6	1	104	127
8	1	64	-78
10	1	59	-66
12	1	52	32
2	2	28	-14
4	2	129	133
6	2	0	-15
8	2	45	-33
10	2	47	50
2	3	60	71
4	3	69	-70
6	3	69	-80
8	3	50	52
10	3	50	45
2	4	0	3
4	4	64	-69
6	4	0	12
8	4	0	-22
10	4	0	30
2	5	0	-37
4	5	48	30
6	5	0	-39
8	5	0	-26
2	6	0	0

Where $F_{obs} = 0$, the reflection was not observed.

CALCULATIONS

FOR THE YEAR

Calculated and observed values for the year

Year	Calculated	Observed
1900	1.0000000000	1.0000000000
1901	1.0000000000	1.0000000000
1902	1.0000000000	1.0000000000
1903	1.0000000000	1.0000000000
1904	1.0000000000	1.0000000000
1905	1.0000000000	1.0000000000
1906	1.0000000000	1.0000000000
1907	1.0000000000	1.0000000000
1908	1.0000000000	1.0000000000
1909	1.0000000000	1.0000000000
1910	1.0000000000	1.0000000000
1911	1.0000000000	1.0000000000
1912	1.0000000000	1.0000000000
1913	1.0000000000	1.0000000000
1914	1.0000000000	1.0000000000
1915	1.0000000000	1.0000000000
1916	1.0000000000	1.0000000000
1917	1.0000000000	1.0000000000
1918	1.0000000000	1.0000000000
1919	1.0000000000	1.0000000000
1920	1.0000000000	1.0000000000
1921	1.0000000000	1.0000000000
1922	1.0000000000	1.0000000000
1923	1.0000000000	1.0000000000
1924	1.0000000000	1.0000000000
1925	1.0000000000	1.0000000000
1926	1.0000000000	1.0000000000
1927	1.0000000000	1.0000000000
1928	1.0000000000	1.0000000000
1929	1.0000000000	1.0000000000
1930	1.0000000000	1.0000000000

These data are for the year 1900

The equation may be rewritten as follows:

$$\rho(\text{XYZ}) = \frac{1}{V} \left[F_{(000)} 2 \sum \sum \sum |F_{(\underline{h}\underline{k}\underline{l})}| \cos 2\pi(\underline{h}\underline{X} + \underline{k}\underline{Y} + \underline{l}\underline{Z}) - \alpha_{(\underline{h}\underline{k}\underline{l})} \right],$$

where $\alpha = \arctan B/A$, and B and A are the two components of the structure factor.

If a space group is centrosymmetric, $B = 0$ and therefore $\alpha = 0$, with the following simplification of the formula:

$$\rho(\text{XYZ}) = \frac{1}{V} \left[F_{(000)} 2 \sum \sum \sum F_{(\underline{h}\underline{k}\underline{l})} \cos 2\pi(\underline{h}\underline{X} + \underline{k}\underline{Y} + \underline{l}\underline{Z}) \right].$$

For the space group Gmcm the general electron density formula is represented by the equation:

$$\rho(\text{XYZ}) = \frac{8}{V} \left[\sum \sum \sum_{\substack{\underline{l} = 2n \\ \underline{l} = 2n+1}} \frac{F_{(\underline{h}\underline{k}\underline{l})}}{F_{(\underline{h}\underline{k}\underline{l})}} \cos 2\pi \underline{h}\underline{X} \cos 2\pi \underline{k}\underline{Y} \cos 2\pi \underline{l}\underline{Z} \right. \\ \left. - \sum \sum \sum_{\substack{\underline{l} = 2n \\ \underline{l} = 2n+1}} \frac{F_{(\underline{h}\underline{k}\underline{l})}}{F_{(\underline{h}\underline{k}\underline{l})}} \cos 2\pi \underline{h}\underline{X} \sin 2\pi \underline{k}\underline{Y} \sin 2\pi \underline{l}\underline{Z} \right],$$

(International Tables for X-ray Crystallography, Vol. I, 1952). The formula for the two-dimensional Fourier synthesis will reduce to the following:

$$\rho(\text{YZ}) = \frac{4}{A} \left[\sum \sum_{\substack{\underline{l} = 2n \\ \underline{l} = 2n+1}} \frac{F_{(0\underline{k}\underline{l})}}{F_{(0\underline{k}\underline{l})}} \cos 2\pi \underline{k}\underline{Y} \cos 2\pi \underline{l}\underline{Z} \right. \\ \left. - \sum \sum_{\substack{\underline{l} = 2n \\ \underline{l} = 2n+1}} \frac{F_{(0\underline{k}\underline{l})}}{F_{(0\underline{k}\underline{l})}} \sin 2\pi \underline{k}\underline{Y} \sin 2\pi \underline{l}\underline{Z} \right].$$

Intervals Y and Z were chosen such that their values, as a fraction of the unit cell, would be equivalent in Angstroms. The interval of Y was chosen as 1/100 of b_0 and that of Z as 1/42 of c_0 . Each interval in the Y and Z

The equation may be written as follows:

$$9(x^2) - \frac{1}{4} \left[\frac{1}{(x^2)} \right] = (x^2)$$

where $\lambda =$ given and $\mu =$ given

the resulting factor,

If a space between x and x^2 is

lets $\lambda = 0$, with the result that

$$9(x^2) - \frac{1}{4} \left[\frac{1}{(x^2)} \right] = (x^2)$$

For the space between x and x^2 is

letting in the result of the

$$9(x^2) - \frac{1}{4} \left[\frac{1}{(x^2)} \right] = (x^2)$$

the result of the

(International Table for

1952). The formula for

will reduce to the

$$9(x^2) - \frac{1}{4} \left[\frac{1}{(x^2)} \right] = (x^2)$$

the result of the

International Table for

Integers 1 and 2 are

as a fraction of the

Integers. The interval of

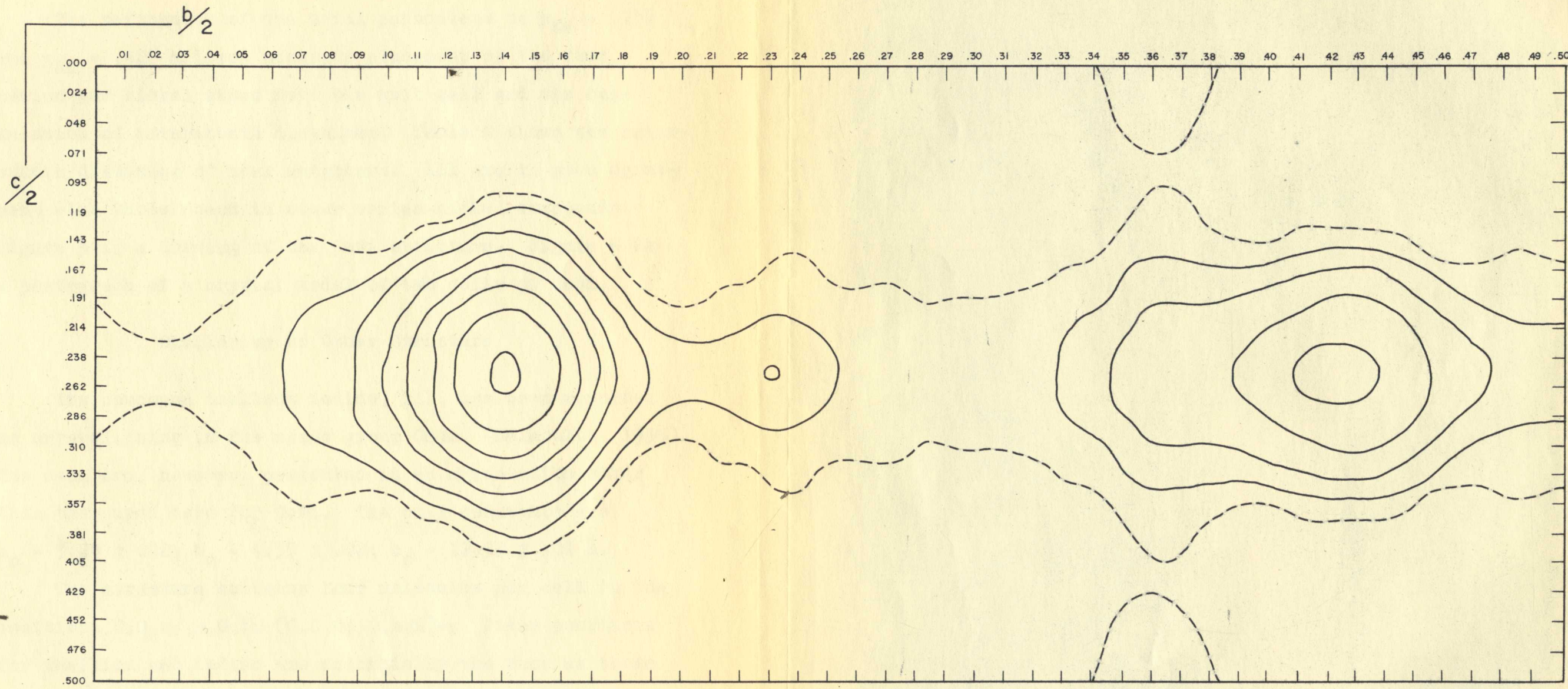
and that of 1 and 2

direction was, therefore, $.104 \text{ \AA}$. Calculations were made over one-quarter of the area b_0xc_0 ; the remaining portions of the area being equivalent due to symmetry requirements.

The Fourier synthesis was made at the Los Alamos Scientific Laboratory using the Maniac II computer. A Fourier projection from these computations is shown in Figure 4. The elongation of the peaks is probably due to the limited nature of the data, since only 36 reflections of the type $0k\ell$ were available. The parameters $y_{Ce} = .14$ and $y_{Ni} = .425$ are in good agreement with those obtained from the least squares refinement.

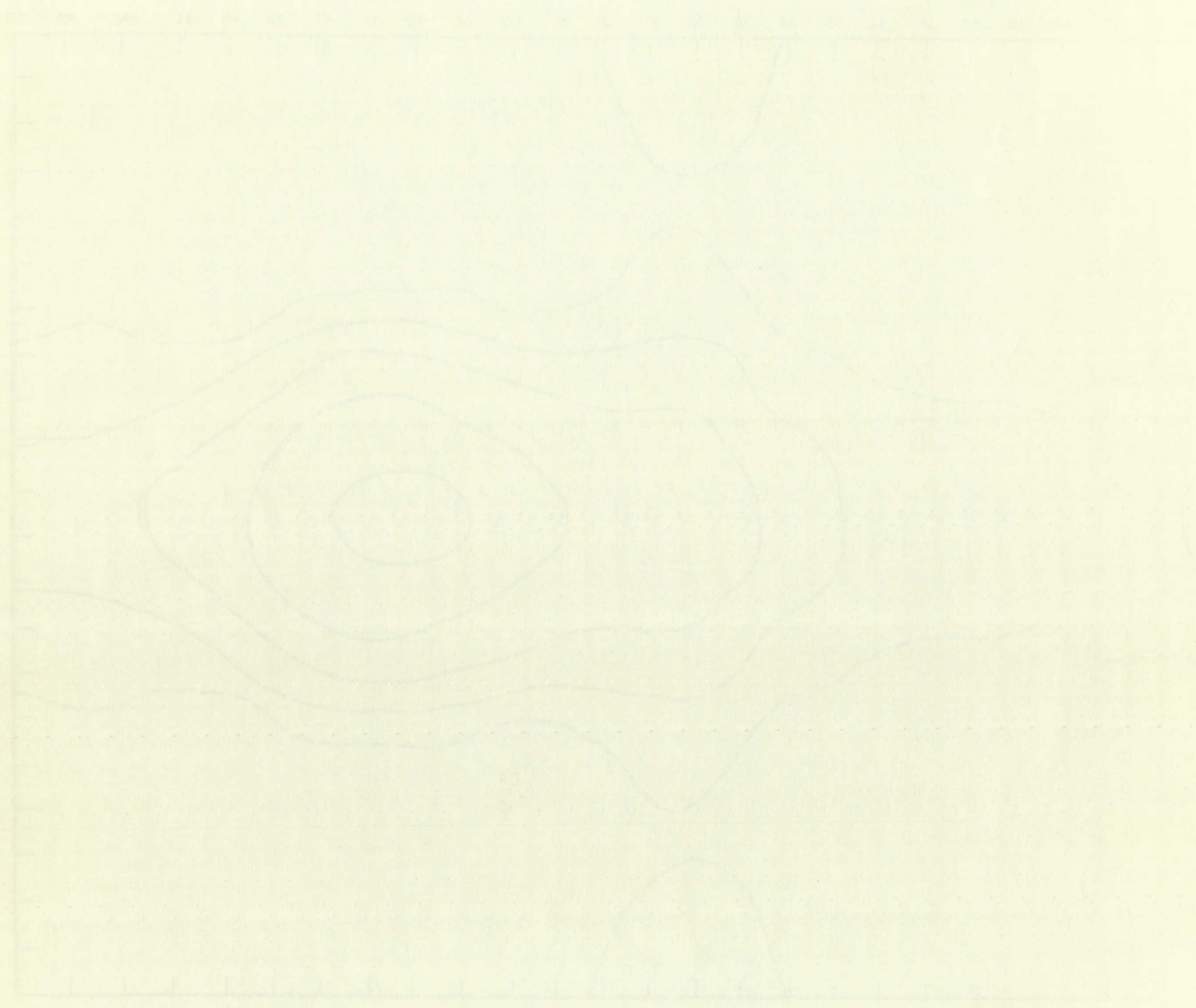
1952

direction was...
over one-quarter...
of the area...
the...
Scientific...
...
Figures...
one...
of the...
and...
from the...



Contour Interval- 40 Electrons/Å
Zero Contour Dashed

FIGURE. 4 - FOURIER PROJECTION OF CeNi ON (100)



SECTION OF CANTON ON FLOOR

DISCUSSION OF STRUCTURE

Interatomic Distances

The refinement of the trial parameters to $y_{\text{Ce}} = .139$ and $y_{\text{Ni}} = .427$ allowed accurate placement of the four cerium and nickel atoms into the unit cell and the calculation of interatomic distances. Table X shows the interatomic distances of near neighbors. All are in good agreement with those found in other cerium-nickel compounds. Figure 5 is a drawing of the CeNi structure. Figure 6 is a photograph of a crystal model of two cells of CeNi.

Similarity to Other Structure

The compound thallos iodide, TlI, has been reported as crystallizing in the space group Cmc₂m, (Helmholtz, 1936). The data are, however, presented in an orientation other than that used here for CeNi. The cell constants are $a_0 = 5.24 \pm .02$; $b_0 = 4.57 \pm .02$; $c_0 = 12.92 \pm .01 \text{ \AA}$.

The structure contains four molecules per cell in the positions $0,0,z$; $\frac{1}{2},0,\bar{z}$; $(0,0,0; 0,\frac{1}{2},\frac{1}{2})_+$. These positions for thallium and iodine are essentially the same as those for cerium and nickel in the CeNi structure with the b and c axes interchanged. The parameters in the thallos iodide structure are $z_{\text{Tl}} = .392 \pm .002$ and $z_{\text{I}} = .133 \pm .002$. The sizes of thallium and cerium, 1.70 and 1.82 \AA respectively,

REV
DINO
CORRECTION

The following is a list of the specimens
and their locations. The specimens are
located in the following locations:
The specimens are located in the following locations:
The specimens are located in the following locations:
The specimens are located in the following locations:
The specimens are located in the following locations:

LIST OF SPECIMENS

The specimens are listed in the following order:
as they appear in the field. The specimens are
The data are, however, presented in the following order:
than that they have been found. The specimens are
 $a = 2.5 \pm 1.0$ (approximate values)
The specimens are listed in the following order:
positions 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0
for the first and last specimens. The specimens are
for certain and also for the specimens. The specimens are
a case intercalated. The specimens are listed in the following order:
structure and the specimens are listed in the following order:
state of the specimens and the specimens are listed in the following order:

REV
DINO
CORRECTION

Table X

Interatomic distances in CeNi

	Distance, Å.
Ce ₁ to Ce ₁	3.77
Ce ₁ '	4.37
Ce ₂	3.70
Ce ₂ to Ce ₃	3.64
Ce ₁ to Ni ₁	3.01
Ce ₂ to Ni ₁	2.97
Ni ₂	2.91
Ni ₁ to Ni ₁	3.77
Ni ₂	2.66

TABLE I

INTRACELLULAR DISTANCES IN CELL

The following table shows the intracellular distances in cell...

Table I

INTRACELLULAR DISTANCES IN CELL

Distance, A.

Cell to Cell 3.77

Cell to Cell 3.87

Cell 3.70

Cell to Cell 3.64

Cell to Cell 3.01

Cell to Cell 2.97

Cell 2.91

Cell to Cell 3.77

Cell 2.66

Cell to Cell 3.77

Cell to Cell 3.77

Cell to Cell 3.77

Cell to Cell 3.77

Cell to Cell 3.77

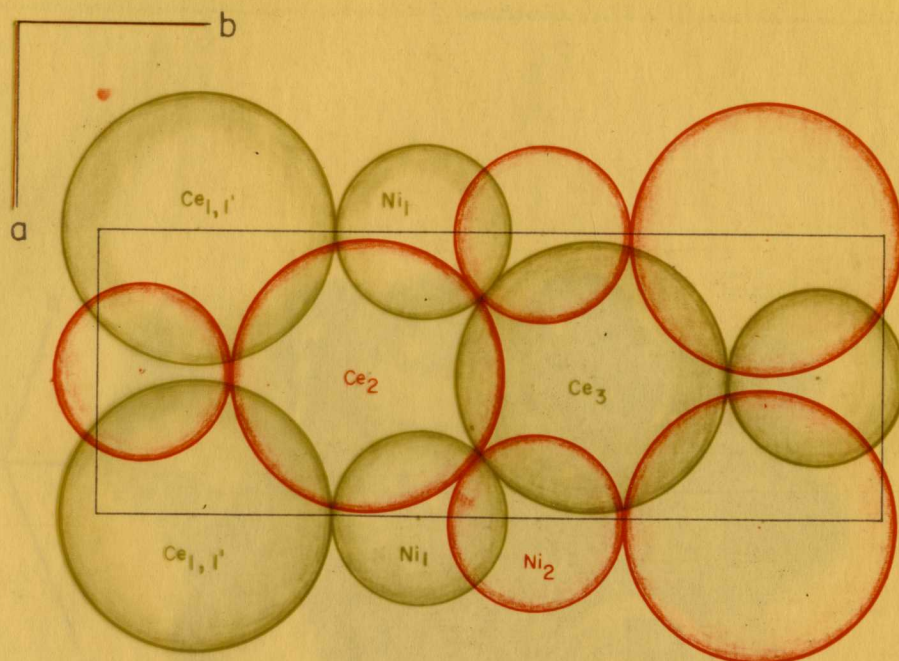
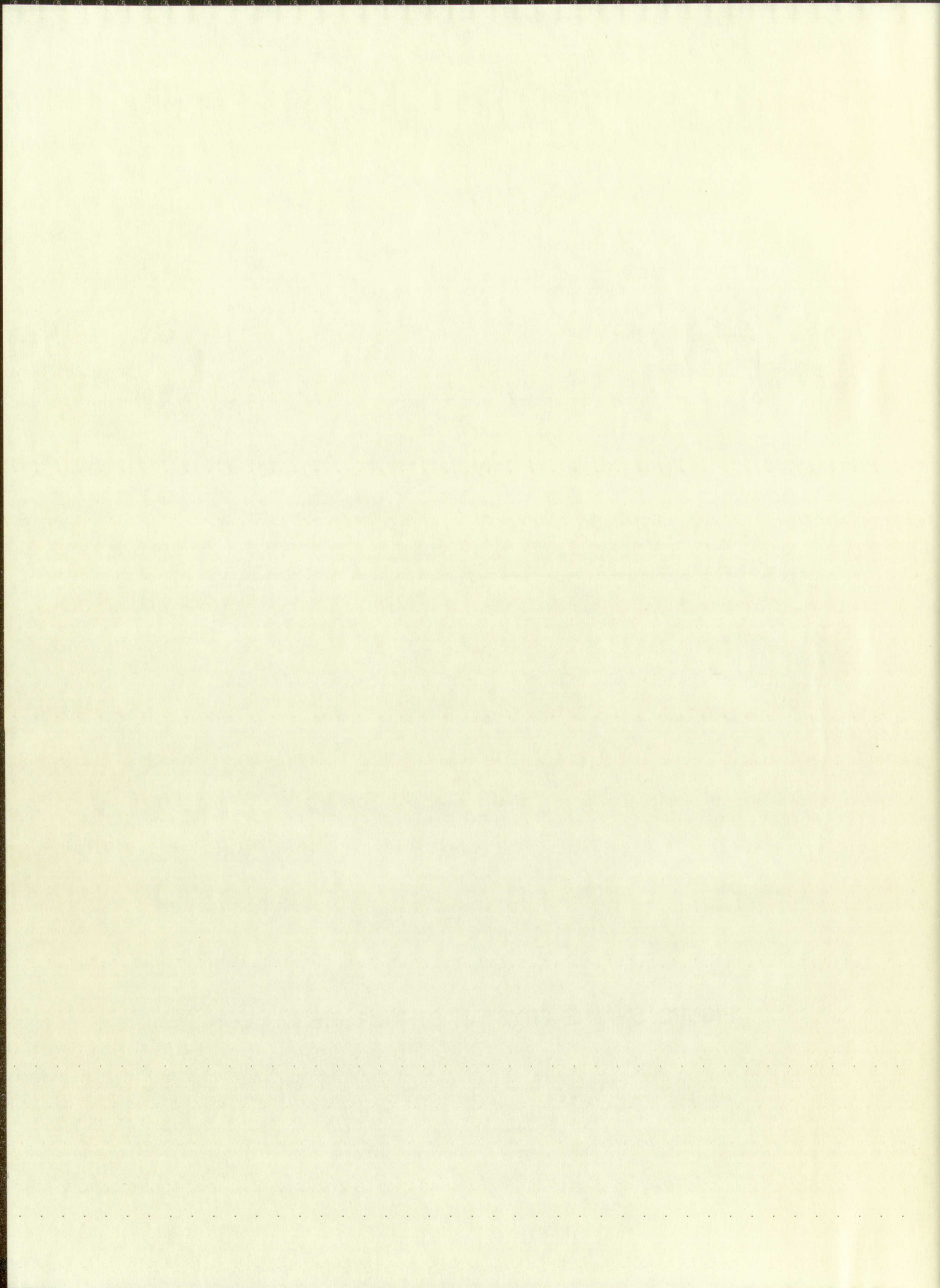


FIGURE. 5 - THE CRYSTAL STRUCTURE OF Ce Ni



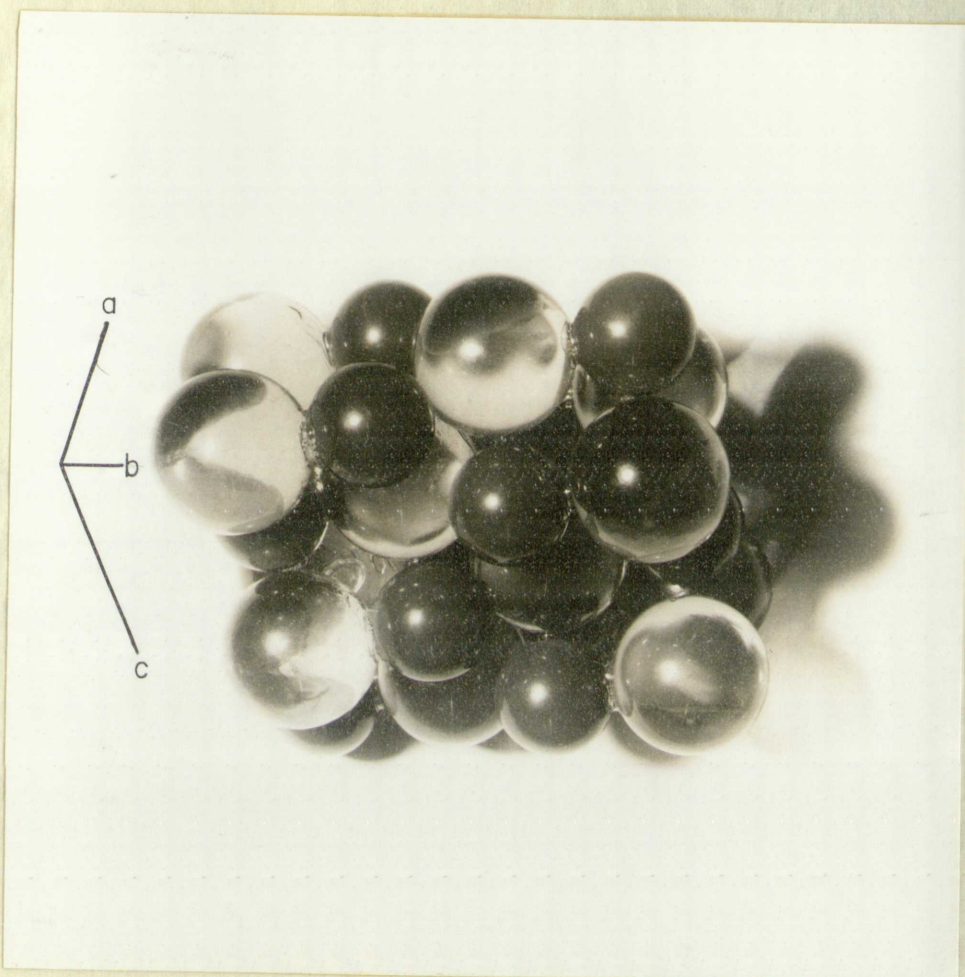


FIGURE 6 -- PHOTOGRAPH OF A CRYSTAL MODEL OF CeNi.
TWO CELLS ARE SHOWN.

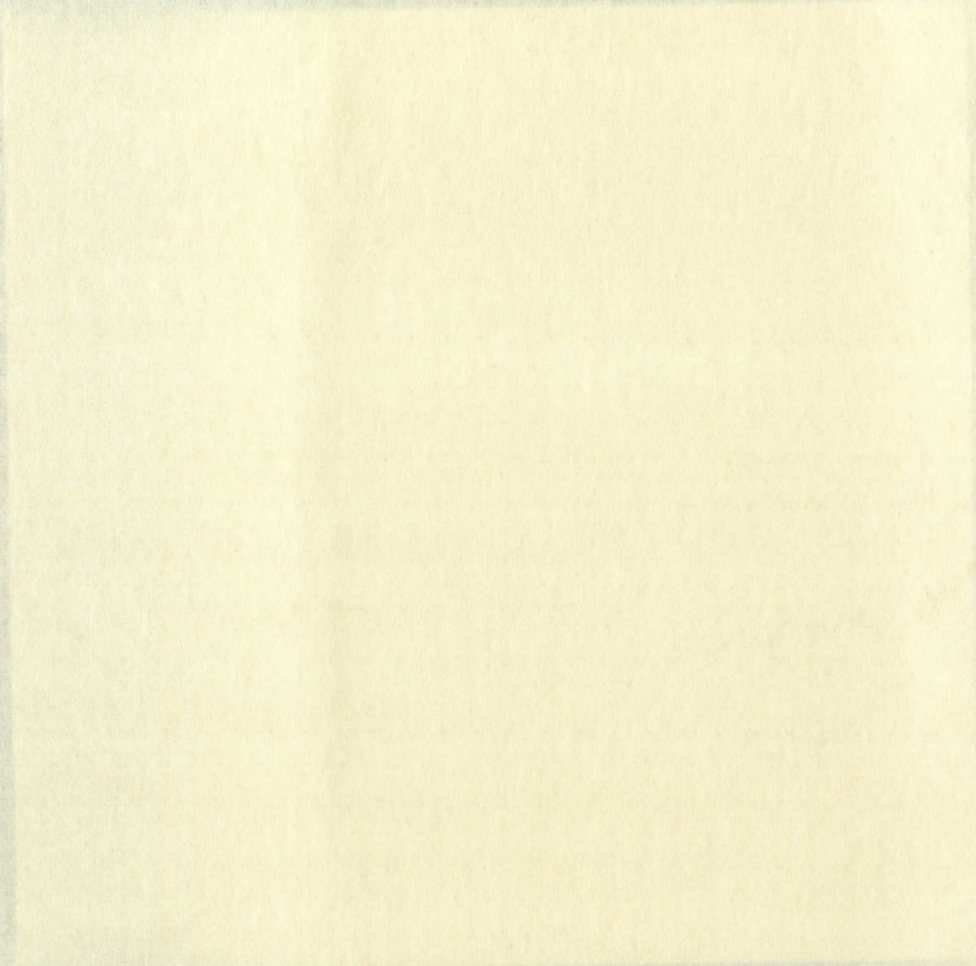


FIGURE 5 - PRODUCTION OF ...

...
...
...

...
...

...
...

compare favorably as do those of iodine and nickel, 1.36 and 1.24 Å respectively. The parameters in both compounds agree closely.

Physical properties

Fresh surfaces of CeNi have a silver-gray color with a metallic luster. Upon prolonged exposure to the air the surface becomes dull and tarnished. The compound is heavy, having an observed specific gravity of 7.51.

Crystal faces were not observed but two cleavages, (010) perfect and (100) good, were observed. The surfaces of the samples were scratched easily with a needle and the estimated hardness is about 4 on the Moh's scale of hardness.

CONFIDENTIAL

... ..
... ..
... ..

... ..
... ..
... ..

... ..
... ..
... ..

CONFIDENTIAL

BIBLIOGRAPHY

- Buerger, M. J., 1941, Numerical structure factor tables: Geol. Soc. America Spec. Paper 33, 118 p.
- _____, 1942, X-ray Crystallography: New York, John Wiley and Sons, 531 p.
- Cromer, D. T., and Olsen, C. E., 1959, The crystal structure of PuNi_3 and CeNi_3 : Acta Cryst., in press.
- _____, and Larson, A. C., 1959, The crystal structure of Ce_2Ni_7 : Acta Cryst., in press.
- Dragsdorf, R. D., 1953, Crystal alignment on the Weissenberg goniometer: Acta Cryst., v. 6, p. 220.
- Goldschmidt, V. M., 1929, Crystal structure and chemical constitution: Trans. Fara. Soc., v. 25, p. 253.
- Helmholtz, L., 1936, The crystal structure of the low temperature modification of thallic iodide: Z. für Kristallographie, v. 95A, p. 129.
- Internationale Tabellen zur Bestimmung von Krystallstrukturen, 1935, Berlin, Gebrüder Borntraeger.
- International Tables for X-ray Crystallography, 1952, v. I, Birmingham, Kynoch Press, 558 p.
- Lipson, H., and Cochran, W., 1953, The Determination of Crystal Structures: London, G. Bell and Sons, 345 p.
- Nowotny, H., 1942, Die Kristallstrukturen von Ni_5Ce , Ni_5La , Ni_5Ca , Cu_5La , Zn_5La , Zn_5Ca , Ni_2Ce , MgCe , MgCa , und MgSi : Z. für Metallkunde, v. 34, p. 247-253.
- Rankama, K., and Sahama, Th. G., 1952, Geochemistry: Chicago, University of Chicago Press, 912 p.
- Viervoll, H., and Ögrim, O., 1949, An extended table of atomic scattering factors: Acta Cryst., v. 2, p. 277-279.
- Vogel, R., 1947, Über die Systeme Cer-Nickel, Lanthan-Nickel, Praseodym-Nickel, und Cer-Kobalt: Z. für Metallkunde, v. 38, p. 97-103.



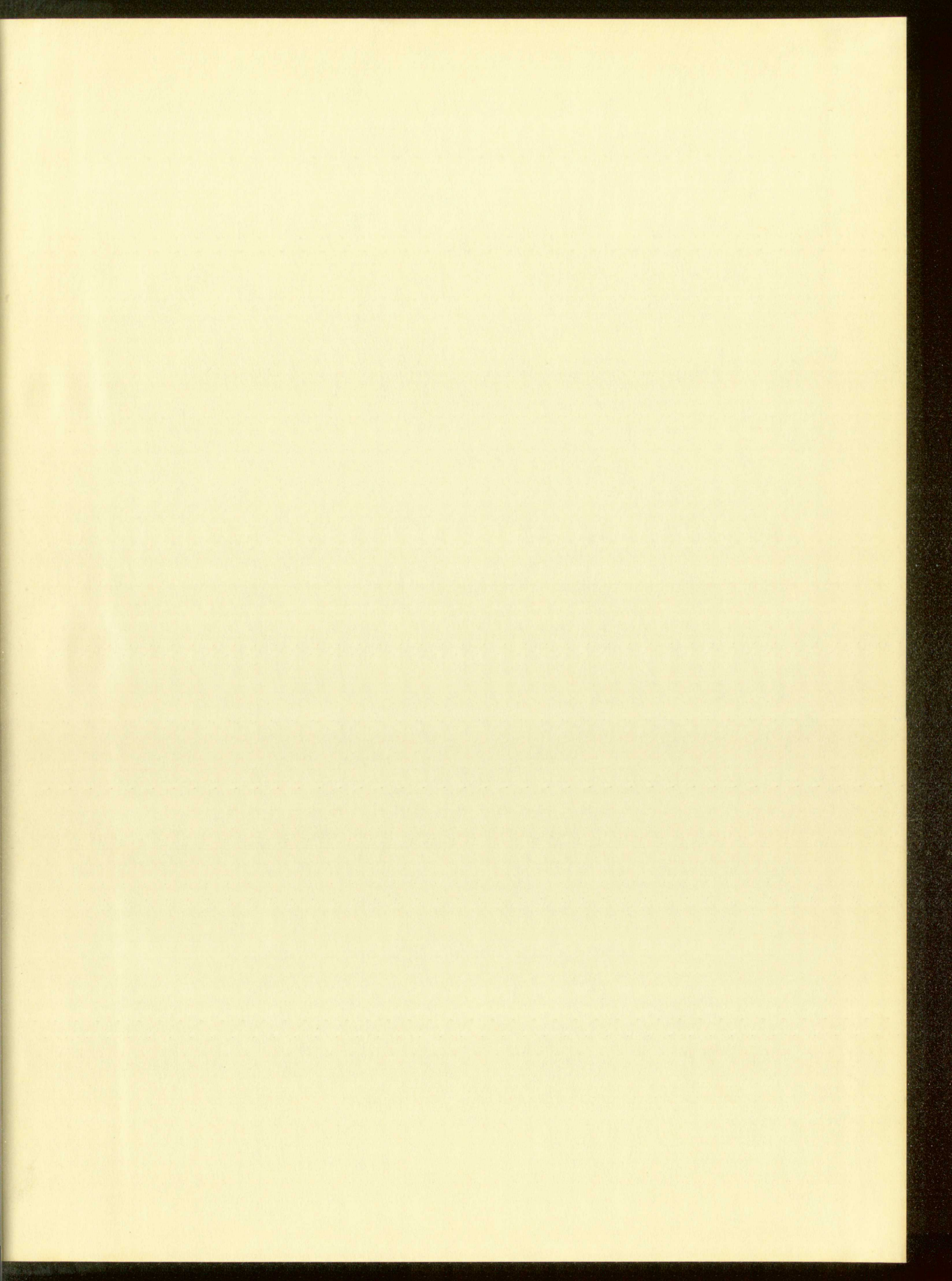
[The following text is extremely faint and mirrored, likely bleed-through from the reverse side of the page. It appears to be a list of names and dates, possibly a table of contents or an index.]

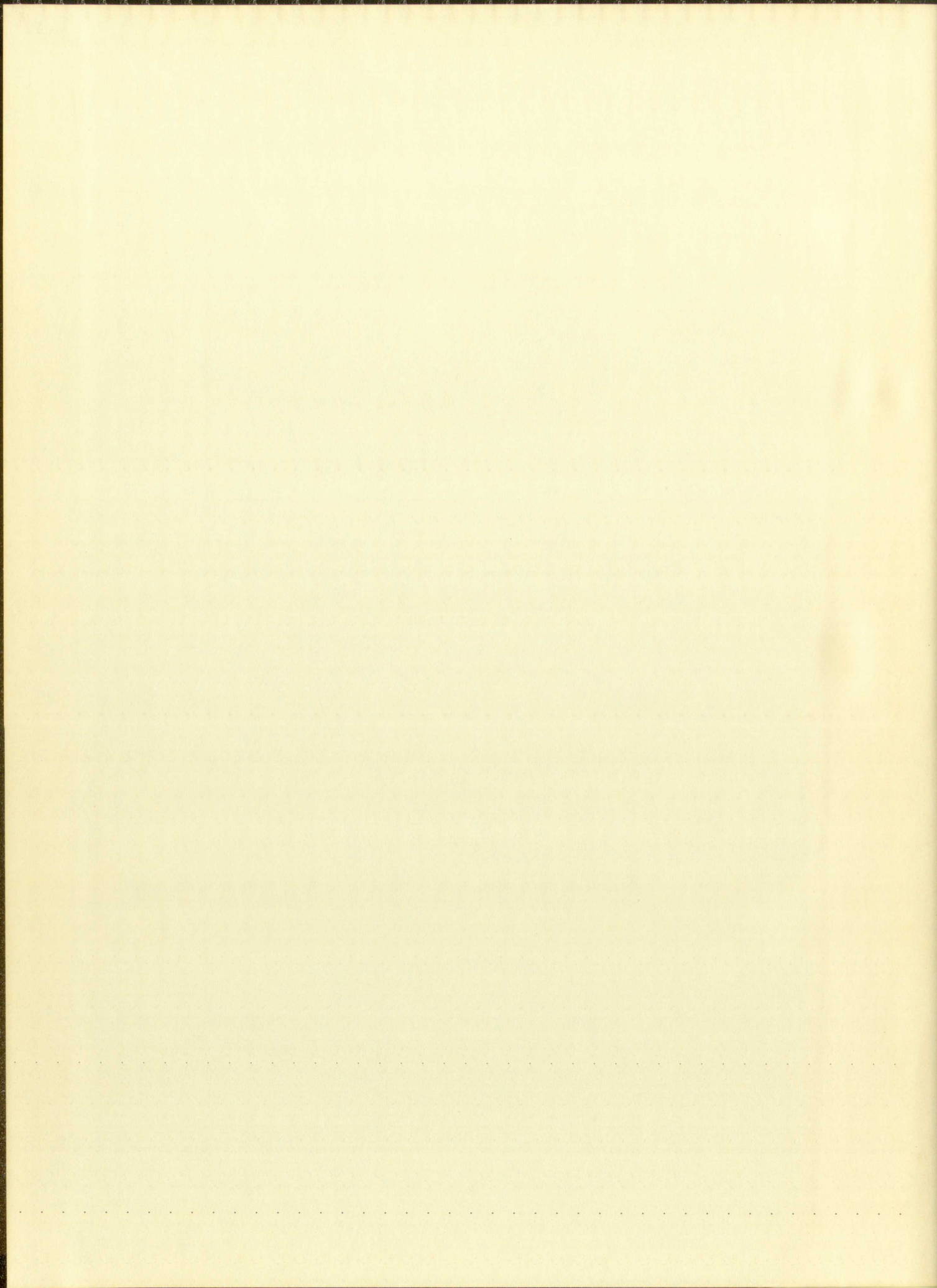
Berg, ...
1922, ...
Gross, ...
1923, ...
Goldstein, ...
Helmholtz, ...
International ...
Lisson, ...
Novotny, ...
Rakman, ...
Vogel, ...

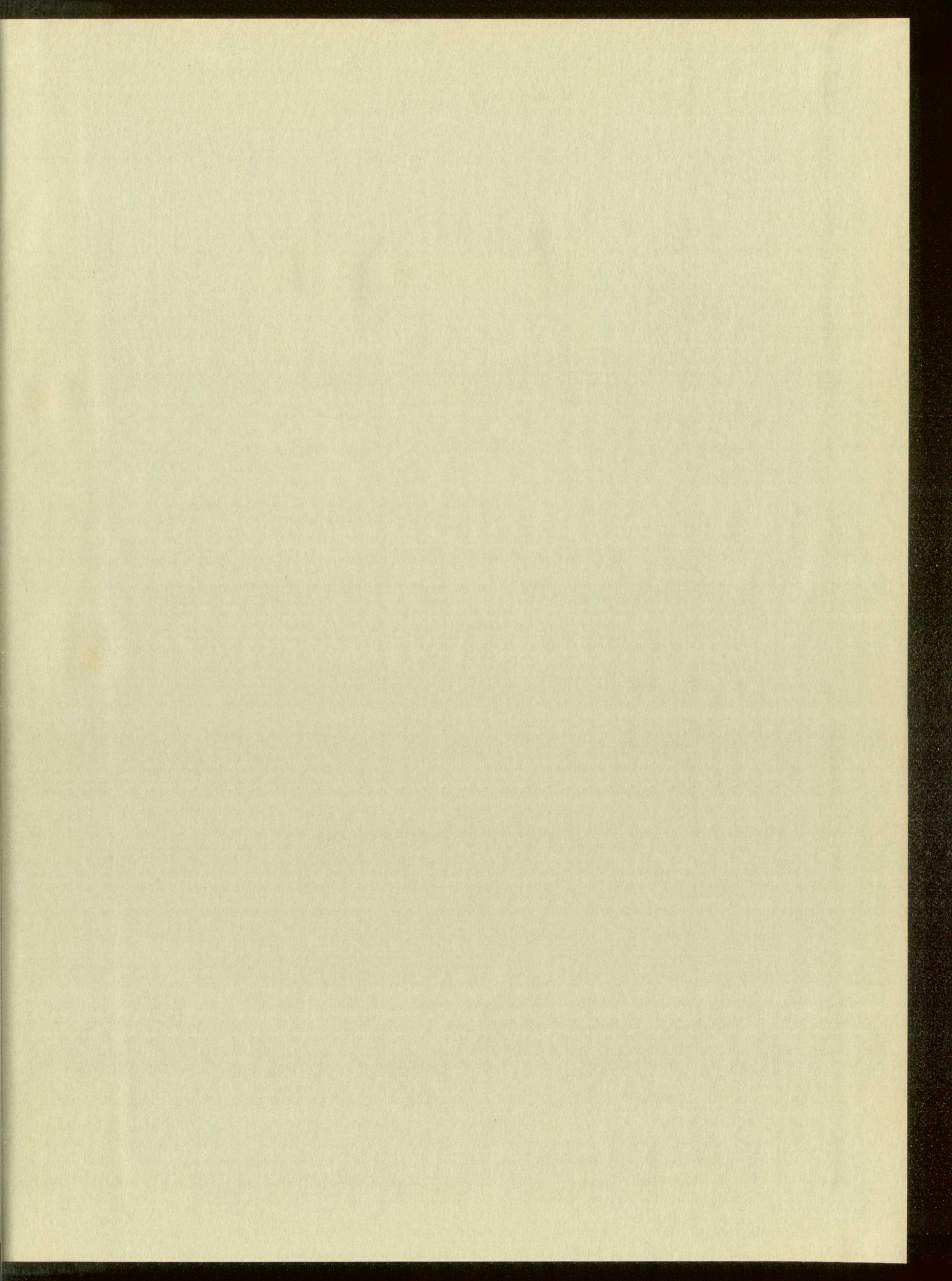
189
WOLFE
COMPARABLE
BOND
MADE IN
ENGLAND
COTTING & COY

WATSON
CORPORATION
BOSTON
MASSACHUSETTS
U.S.A.

WATSON CORPORATION








IMPORTANT!

Special care should be taken to prevent loss or damage of this volume. If lost or damaged, it must be paid for at the current rate of typing.

Date Due		
MAY 11 1960		
DEC 20 1960		
APR 3 - 1962		
MAR 13 1962		
	PRINTED	IN U. S. A.

