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CRYSTAL STRUCTURE OF CE NI - FINNEY

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

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1959

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

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DATE May 20, 1959

Thesis committee

Abraham Rosenzweig
CHAIRMAN

J. Paul Fitzsimmons

W. E. Elston

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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 Cmcm with $a_o = 3.77 \pm 0.01$, $b_o = 10.46 \pm 0.02$, $c_o = 4.37 \pm 0.01$ Å. The cell formula is Ce_4Ni_4. The observed density is 7.51 grams/cm^3 and the calculated density is 7.65 grams/cm^3, 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, $0,y,\frac{1}{4}$; $0,\bar{y},\frac{3}{4}$; $(+\ 0,0,0;\ \frac{1}{2},\frac{1}{2},0)$; $y_{Ce} = .139 \pm .002$, $y_{Ni} = .428 \pm .004$. 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 thallous iodide. Two cleavage directions are present, (010) perfect and (100) good.

THE CRYSTAL STRUCTURE OF CeNi

Abstract.

X-ray diffraction methods were used to determine the cell constants and structure of CeNi. The cell is orthorhombic. The [illegible] [illegible] [illegible] [illegible] $a_0 = 3.77 \pm 0.01$, $b_0 =$ [illegible], $c_0 =$ [illegible]. The cell formula is Ce_4Ni_4. The observed density is 7.31 grams/cm^3 and the calculated density is [illegible] [illegible] a deviation of 1.2%.

The trial parameters [illegible] were refined by the least squares method. The [illegible] gives close agreement [illegible] cerium and nickel in the four-fold [illegible] ($\pm$ 0,0,0; ½,½,0); [illegible]. The minimum interatomic distances [illegible] 2.65 Å for Ni-Ni, and [illegible] Å [illegible].

The structure is similar to [illegible]. Two cleavage directions are [illegible] (100) good.

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.

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 Fd3m, $a_o = 7.178$ Å, and cell contents Ce_8Ni_{16}. $CeNi_5$ is hexagonal with space group P6/mmm, $a_o = 4.864$, $c_o = 3.996$ Å, with one formula weight per cell.

assistance was [illegible]

Don T. Cromer, Los Alamos Scientific Laboratory, and [illegible] Abraham Rosenzweig, [illegible] of [illegible] New Mexico.

The problem was selected for [illegible] by the Los Alamos Scientific Laboratory.

PREVIOUS WORK

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The crystal structures [illegible] mined by Nowotny (1942). [illegible] space group [illegible] a = [illegible] $CeNi_5$ is hexagonal with [illegible] c_o = 3.956 Å, with [illegible]

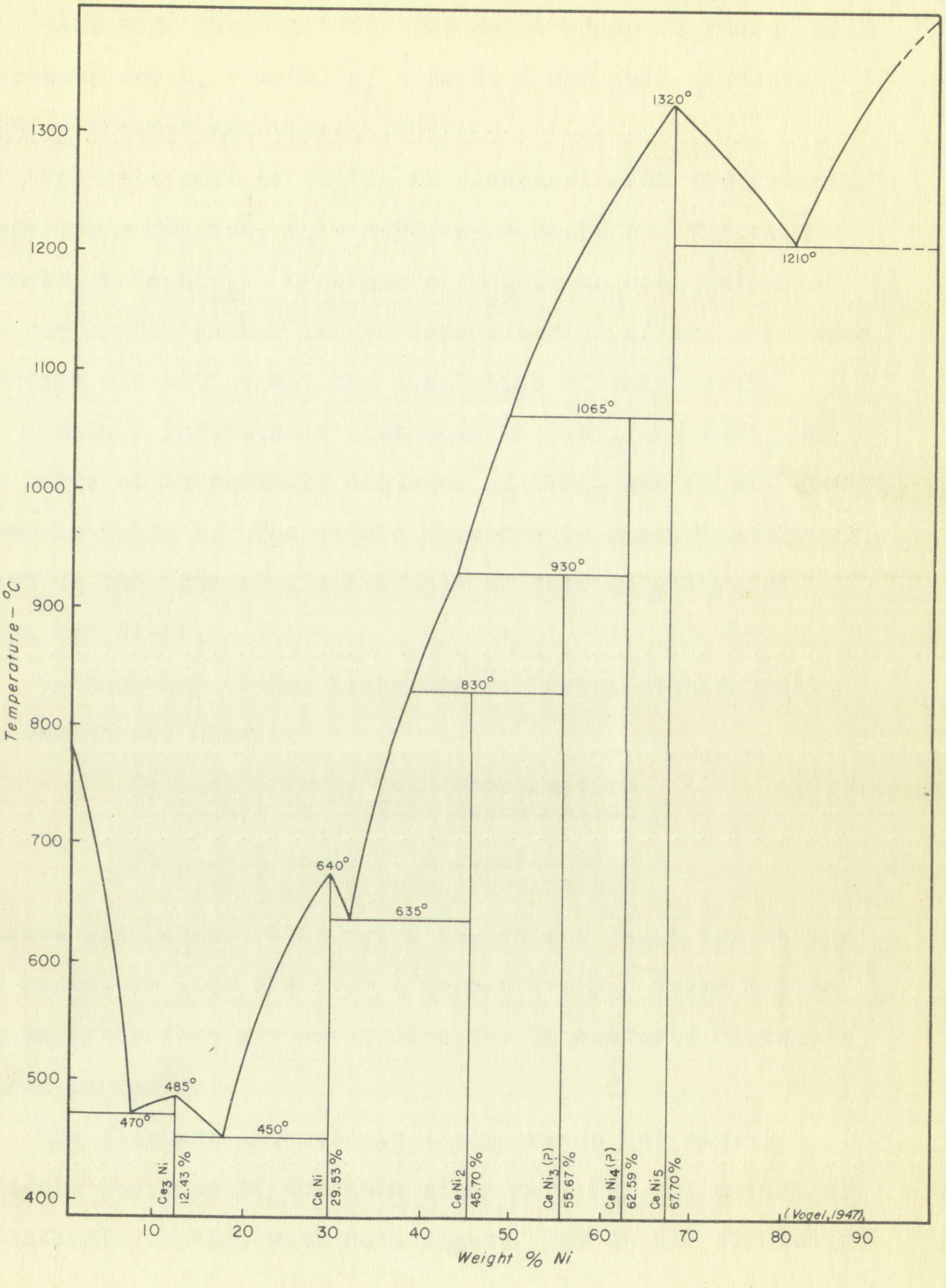


FIGURE. 1 - PHASE DIAGRAM OF THE CERIUM - NICKEL SYSTEM

$CeNi_3$ is hexagonal with the space group $P6_3/mmc$. Cell constants are $a_o = 4.98$, $c_o = 16.54$ Å and cell contents Ce_6Ni_{18} (Cromer and Olsen, 1959).

The unit cell of Ce_2Ni_7 is hexagonal with the probable space group $P6_3/mmc$, $a_o = 4.98$, $c_o = 24.52$ Å. The cell formula is Ce_8Ni_{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 Å	in 12 fold coordination
	1.76 Å	in 8 fold coordination
Ni	1.24 Å	in 12 fold coordination
	1.21 Å	in 8 fold coordination

Rankama and Sahama (1952) give the atomic radii for cerium and nickel as 1.82 and 1.24 Å 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

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

The structures of CeNi and Ce_3Ni have not been previously determined.

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

EXPERIMENTAL METHODS

Preparation of Samples

Two samples of CeNi and one sample of Ce_3Ni 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 Ce_3Ni 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.

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 $\underline{hk}0$ 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 $0\underline{k\ell}$ 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

X-ray Diffraction Studies

Selection of a suitable x-ray [illegible] use with CsAl [illegible] involved [illegible] of the elements involved. [illegible] number element, [illegible] high. The use of X-rays [illegible] but does not eliminate [illegible] ignored however, [illegible]

The optimum [illegible] .711 Å, was found [illegible] for Cu Ka radiation [illegible] of approximately [illegible] and Mo Ka radiation [illegible] used for the initial [illegible] space group [illegible] strong reflections [illegible] to be lined up [illegible] by the method of [illegible]

For intensity measurements, [illegible] oriented for [illegible] tions were badly elongated. [illegible] orientation gave [illegible] parallel to the [illegible]

Three sheets of [illegible] in order to [illegible] reflections, and [illegible] 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 $0k\ell$ 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 hours. The sixty-hour exposure time proved to be [illegible] too short and eighty hours [illegible] ures set at two hundred and forty hours. [illegible] yielded reflections of [illegible].

The intensities of [illegible] reflections were [illegible] by comparison with a scaled [illegible]. A suitable strong spot [illegible] the θ angle and [illegible] measured. All other [illegible] were [illegible] the crystal was oscillated [illegible] oscillations [illegible] the film, with the [illegible] set calculated [illegible] sity of this [illegible] graph was [illegible] with the scale. [illegible] upon the calculated [illegible] the posi-tion of the film.

Because crystals [illegible] tion occurs over [illegible] points have a finite [illegible] sphere of reflection. [illegible] measure of this time. [illegible] partially polarized. [illegible] this partial polarization [illegible] 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).

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:

$$a_o = 3.77\ \text{Å} \pm .01$$

$$b_o = 10.46\ \text{Å} \pm .02$$

$$c_o = 4.37\ \text{Å} \pm .01.$$

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 0*kℓ*, 1*kℓ*, 2*kℓ*, *hk*0, *hk*1 and *hk*2 and all reflections indexed. Tables II and III list the reflections observed using Cu Kα and Mo Kα respectively. Reflections of the type *hkℓ* were observed only with *h*+*k* = 2n. In addition, in *h*0*ℓ* reflections, only those where *h* = 2n, *ℓ* = 2n were observed. A summary of the observed extinctions follows:

hkℓ	*h*+*k* = 2n
0*kℓ*	(*k* = 2n)
*h*0*ℓ*	*ℓ* = 2n; (*h* = 2n)
*hk*0	(*h*+*k* = 2n)
*h*00	(*h* = 2n)
0*k*0	(*k* = 2n)
00*ℓ*	(*ℓ* = 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

Table II

Observed reflections of CeNi, Cu Kα.

hk0 photograph

200	(s)	110	(w)
400	(s)	130	(m)
040	(s)	170	(s)
060	(vvw)	1110	(s)
080	(m)	240	(w-m)
0100	(m-s)	2100	(w-m)
0120	(vvw)	2120	(w)
		310	(w)
		330	(m)
		370	(m)
		440	(m-s)

hkl photograph

021	(s)	221	(m)
041	(s)	241	(w)
061	(s)	261	(vw)
081	(s)	281	(vvw)
0101	(s)	2101	(m)
0121	(m-s)	2121	(m-s)
111	(m)	311	(s)
131	(w-m)	331	(m)
151	(w)	351	(w)
171	(vw)	391	(m)
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 III

Observed reflections of CeNi, Mo Kα.

0*kl* photograph

002	(s)	0101	(m)
004	(m)	0121	(w)
006	(w)	042	(s)
040	(s)	023	(m)
080	(w)	043	(m)
0100	(m)	063	(m)
0140	(w)	083	(w-m)
021	(s)	0103	(w)
041	(s)	044	(m)
061	(m-s)	045	(vw)

1*kl* photograph

130	(s)	113	(m-s)
170	(m-s)	133	(m)
1110	(w-m)	153	(w)
111	(s)	193	(vw)
131	(s)	134	(w-m)
151	(m)	174	(m)
171	(vw)	115	(vw)
191	(w)	135	(vw)
1131	(vw)		
132	(m-s)		
172	(m)		
1112	(w)		

2*kl* photograph

240	(m)	242	(m-s)
2101	(vvw)	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)		

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

The density of the samples of CeNi was found to be 7.51 grams/cm^3, by the pycnometer method. The volume of the unit cell was calculated as 172.5 Å. 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 Ce_4Ni_4. 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/cm^3, a deviation of 1.8% from the observed density.

noncentrosymmetric [illegible] which were [illegible] using Cmca atomic positions is possible.

The density of the compound, [illegible] was measured as 7.51 grams/cm^3, by the pycnometer method. The volume of the unit cell was calculated as 172.9 Å^3. The number of molecules per cell was calculated from the formula:

$$\frac{\rho N V}{M}$$

where ρ = the observed density, N = Avogadro's number, V = volume of the unit cell and M = molecular weight of the compound, 195.38. n = 3.97 [illegible] and the cell formula is Ce_4Ni_8. The same formula was then used to calculate the density of the compound, and this purpose [illegible] the density, ρ, is calculated [illegible] grams/cm^3, a deviation of 1.0% from the observed density.

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 $\underline{hk\ell}$, with $\underline{\ell} = 2n$ only, and reflections violating this extinction were present.

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

The general and special [illegible]

Cmcm are listed in [illegible]

Tables for X-ray Crystallography [illegible] it is

evident that since only [illegible] and [illegible]

the unit cell, [illegible] special positions

could accommodate [illegible]

of the atoms. [illegible]

tions (a), (b), and (c) [illegible] (c) were

attempted first.

In these positions [illegible]

the c axis. [illegible]

would occupy 7.25 Å. [illegible]

4.98 Å. The c-axis [illegible]

enough to [illegible]

these positions. [illegible]

tions (a) and (b) would [illegible]

hkl with l = 2n only [illegible]

extinction was [illegible].

The remaining four-fold position, (c), [illegible]

which along the [illegible]

Table IV

General and special positions of the space group Cmcm.

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:	$0,0,0;\ 0,0,\frac{1}{2}.$

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:

$$F_{\underline{hk\ell}} = \sum_{n=1}^{N} f_n \cdot e^{2\pi i(\underline{h}x_n+\underline{k}y_n+\underline{\ell}z_n)}$$

The exponential term may be expanded to the form:

$$\cos 2\pi(\underline{h}x+\underline{k}y+\underline{\ell}z) + i\sin 2\pi(\underline{h}x+\underline{k}y+\underline{\ell}z) = A + iB.$$

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

$$A = 16\cdot\cos^2 2\pi\frac{\underline{(h+k)}}{4}\cos 2\pi\underline{h}x\cos 2\pi(\underline{k}y+\underline{\ell}/4)\cos 2\pi(\underline{\ell}z+\underline{\ell}/4)$$

$$B = 0.$$

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

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

$$A = 16\cdot\cos 2\pi\underline{h}x\cos 2\pi\underline{k}y\cos 2\pi\underline{\ell}z,$$

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

$$A = -16\cos 2\pi\underline{h}x\sin 2\pi\underline{k}y\sin 2\pi\underline{\ell}z.$$

These are expressions for atoms in sixteen-fold positions.

The structure factor [illegible] is a function of the relative positions [illegible] and the effective scattering [illegible]. The [illegible] is the atomic scattering factor [illegible] structure amplitude in reference to the [illegible]:

$$F_{hkl} = \sum [illegible]$$

The exponential term may be expressed in the form

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

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

$$A = 16 \cos 2\pi(lz) [illegible]$$

$$B = 0.$$

(International Tables for X-ray Crystallography, [illegible])

For the condition [illegible]

$$A = 16 [illegible]$$

and for the condition [illegible]

$$A = -16 [illegible]$$

These are expressions for which [illegible]

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

$$A = 4\cos 2\pi hx \cos 2\pi ky \cos 2\pi \ell z.$$

For the condition $h+k = 2n$, $\ell = 2n+1$, it becomes:

$$A = -4\cos 2\pi hx \sin 2\pi ky \sin 2\pi \ell z.$$

For reflections of the type $0k\ell$, the expressions are further reduced to:

$$A = 4\cos 2\pi ky \cos \pi\ell/2, \text{ where } h+k = 2n,\ \ell = 2n$$

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

since $h = 0$ and $z = 1/4$.

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

$$F_{0k\ell} = 4\left[f_{Ce}\cos 2\pi ky_{Ce}\cos \pi\ell/2 + f_{Ni}\cos 2\pi ky_{Ni}\cos \pi\ell/2\right]$$

where $h+k = 2n$, $\ell = 2n+1$, it becomes:

$$F_{0k\ell} = -4\left[f_{Ce}\sin 2\pi ky_{Ce}\sin \pi\ell/2 + f_{Ni}\sin 2\pi ky_{Ni}\sin \pi\ell/2\right].$$

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).

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 ¼ 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 ¼ 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 $y_{Ce} = .17$ and $y_{Ni} = .46$ 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 $y_{Ce} = .17$ and $y_{Ni} = .46$ 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

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 0k0 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 0kℓ reflections, together with corrections for the L•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 0k0 reflections only.

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.

Table VI

Observed intensities for 0*kℓ* reflections

k	*ℓ*	I_o	$L\cdot p$	$I_o/L\cdot p$	$\sqrt{I_o/L\cdot p}$
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 0*k*0 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

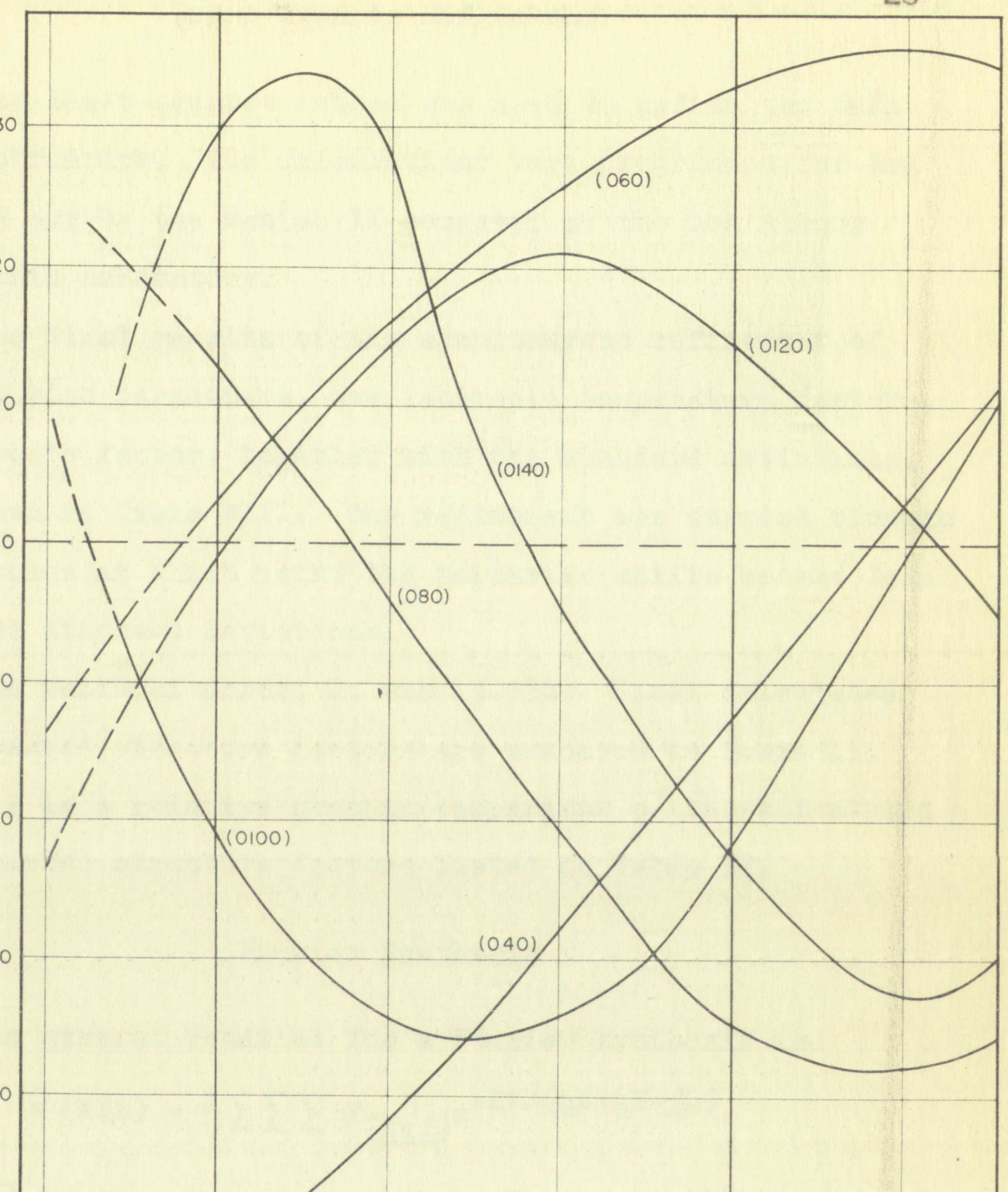


FIGURE. 2 — CALCULATED STRUCTURE FACTORS PLOTTED AGAINST VARYING PARAMETERS.

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:

$$\rho(XYZ) = \frac{1}{V}\sum\sum\sum F_{(\underline{h}\underline{k}\underline{\ell})}e^{-2\pi i(\underline{h}X+\underline{k}Y+\underline{\ell}Z)}$$

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

$$\rho(XYZ) = \frac{1}{V}\Big[F(000)\ 2\sum\sum\sum A_{(\underline{h}\underline{k}\underline{\ell})}\cos 2\pi(\underline{h}X+\underline{k}Y+\underline{\ell}Z) + B_{(\underline{h}\underline{k}\underline{\ell})}\cdot\sin 2\pi(\underline{h}X+\underline{k}Y+\underline{\ell}Z)\Big].$$

Table VIII

Parameters of CeNi from the least squares refinement

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

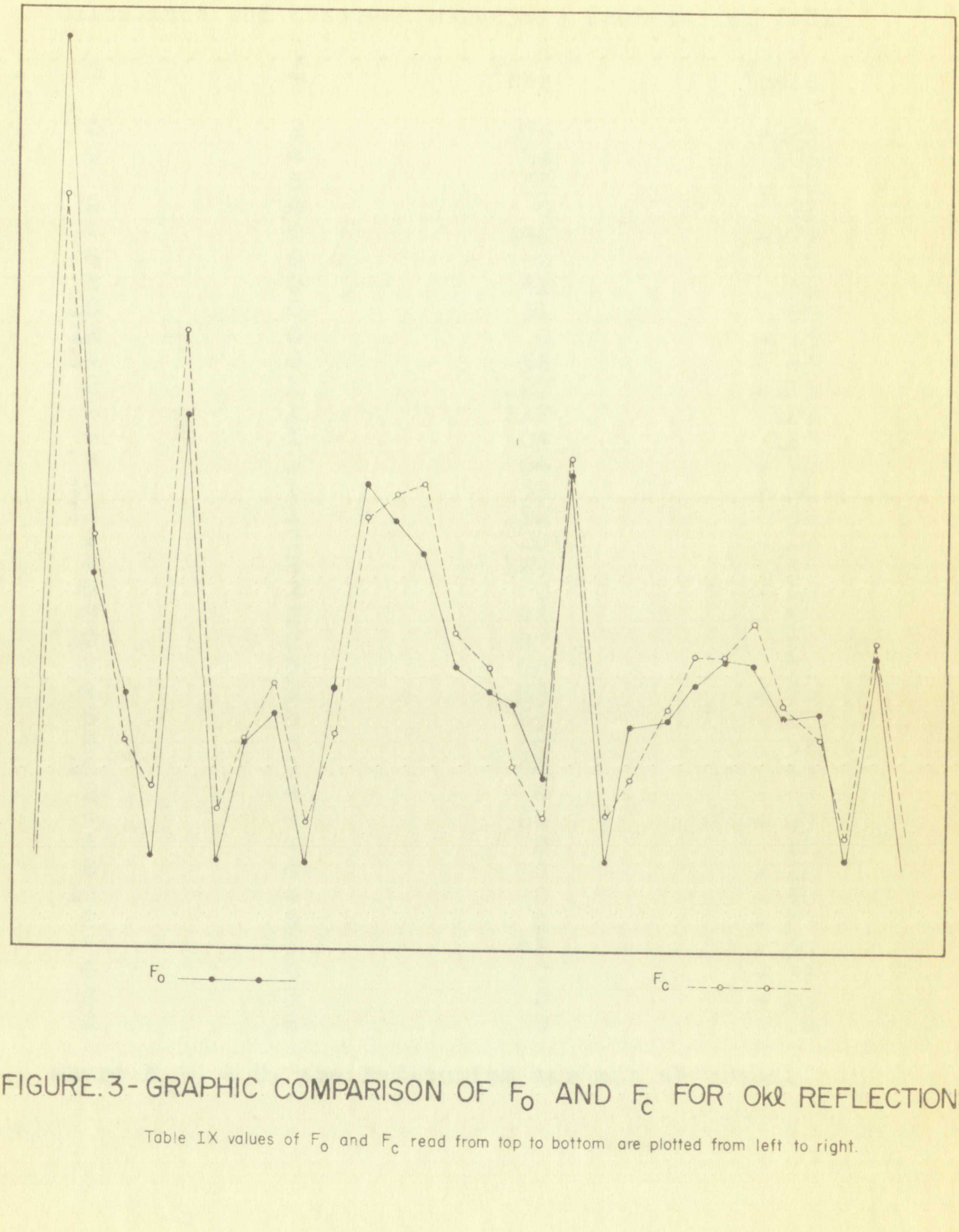


FIGURE. 3 - GRAPHIC COMPARISON OF F_o AND F_c FOR Okℓ REFLECTIONS.

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

Table IX

Calculated and observed structure factors for CeNi

<u>k</u>	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.

The equation may be rewritten as follows:

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

where α = 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:

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

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

$$\rho(XYZ) = \frac{8}{V}\left[\sum\sum\sum \overset{\underline{\ell}\,=\,2n}{F}_{(\underline{hk\ell})}\cos 2\pi\underline{h}X\cos 2\pi\underline{k}Y\cos 2\pi\underline{\ell}Z - \sum\sum\sum \overset{\underline{\ell}\,=\,2n+1}{F}_{(\underline{hk\ell})}\cos 2\pi\underline{h}X\sin 2\pi\underline{k}Y\sin 2\pi\underline{\ell}Z\right],$$

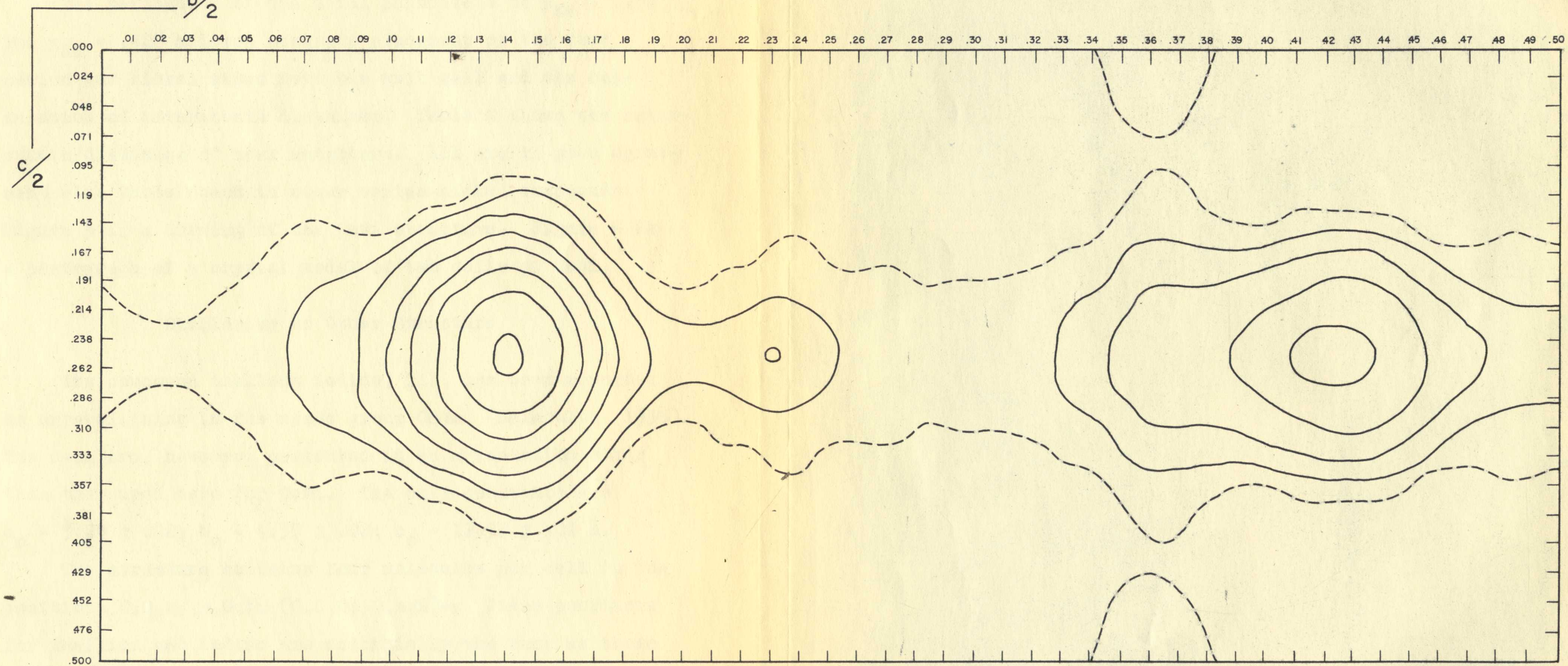
(International Tables for X-ray Crystallography, Vol. I, 1952). The formula for the two-dimensional Fourier synthesis will reduce to the following:

$$\rho(YZ) = \frac{4}{A}\left[\sum\sum \overset{\underline{\ell}\,=\,2n}{F}_{(0\underline{k\ell})}\cos 2\pi\underline{k}Y\cos 2\pi\underline{\ell}Z - \sum\sum \overset{\underline{\ell}\,=\,2n+1}{F}_{(0\underline{k\ell})}\sin 2\pi\underline{k}Y\sin 2\pi\underline{\ell}Z\right].$$

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_o and that of Z as 1/42 of c_o. Each interval in the Y and Z

direction was, therefore, .104 Å. Calculations were made over one-quarter of the area $b_o x c_o$; 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 $\underline{0k\ell}$ were available. The parameters $y_{Ce} = .14$ and $y_{Ni} = .425$ are in good agreement with those obtained from the least squares refinement.



Contour Interval– 40 Electrons/Å

Zero Contour Dashed

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

DISCUSSION OF STRUCTURE

Interatomic Distances

The refinement of the trial parameters to y_{Ce} = .139 and y_{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 thallous iodide, TlI, has been reported as crystallizing in the space group Cmcm, (Helmholtz, 1936). The data are, however, presented in an orientation other than that used here for CeNi. The cell constants are $a_o = 5.24 \pm .02$; $b_o = 4.57 \pm .02$; $c_o = 12.92 \pm .01$ Å.

The structure contains four molecules per cell in the positions 0,0,z; ½,0,$\bar{z}$; (0,0,0; 0,½,½)+. 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 thallous iodide structure are $z_{Tl} = .392 \pm .002$ and $z_I = .133 \pm .002$. The sizes of thallium and cerium, 1.70 and 1.82 Å respectively,

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

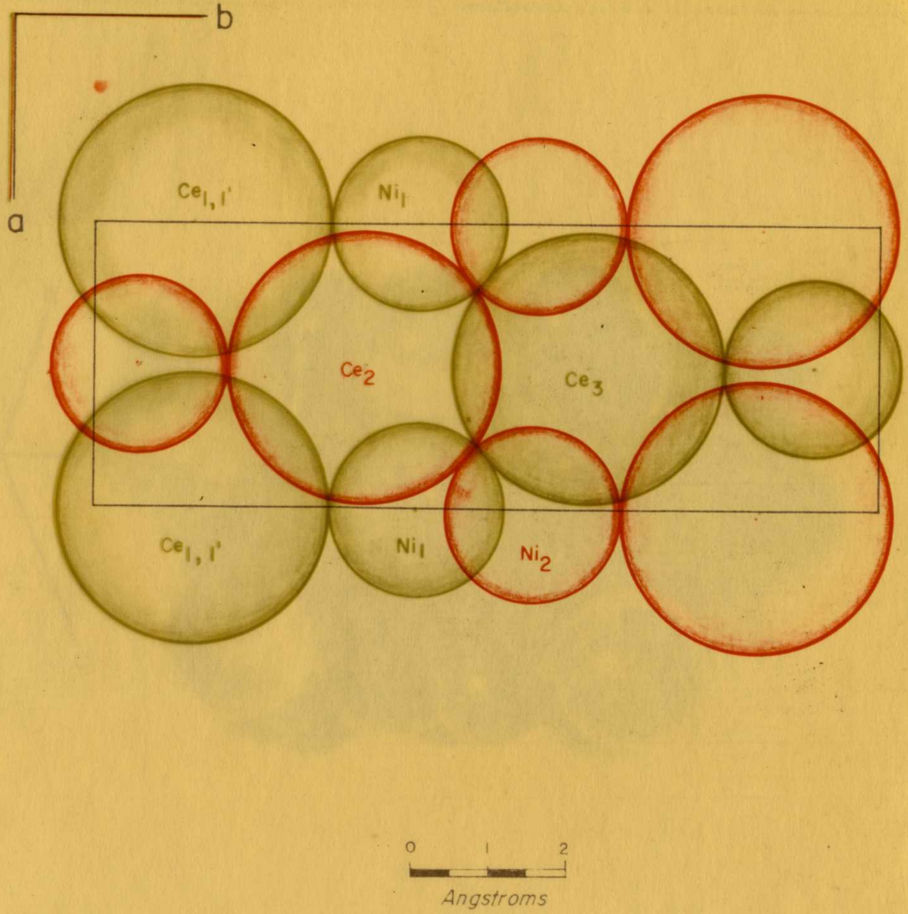


FIGURE. 5 – THE CRYSTAL STRUCTURE OF Ce Ni

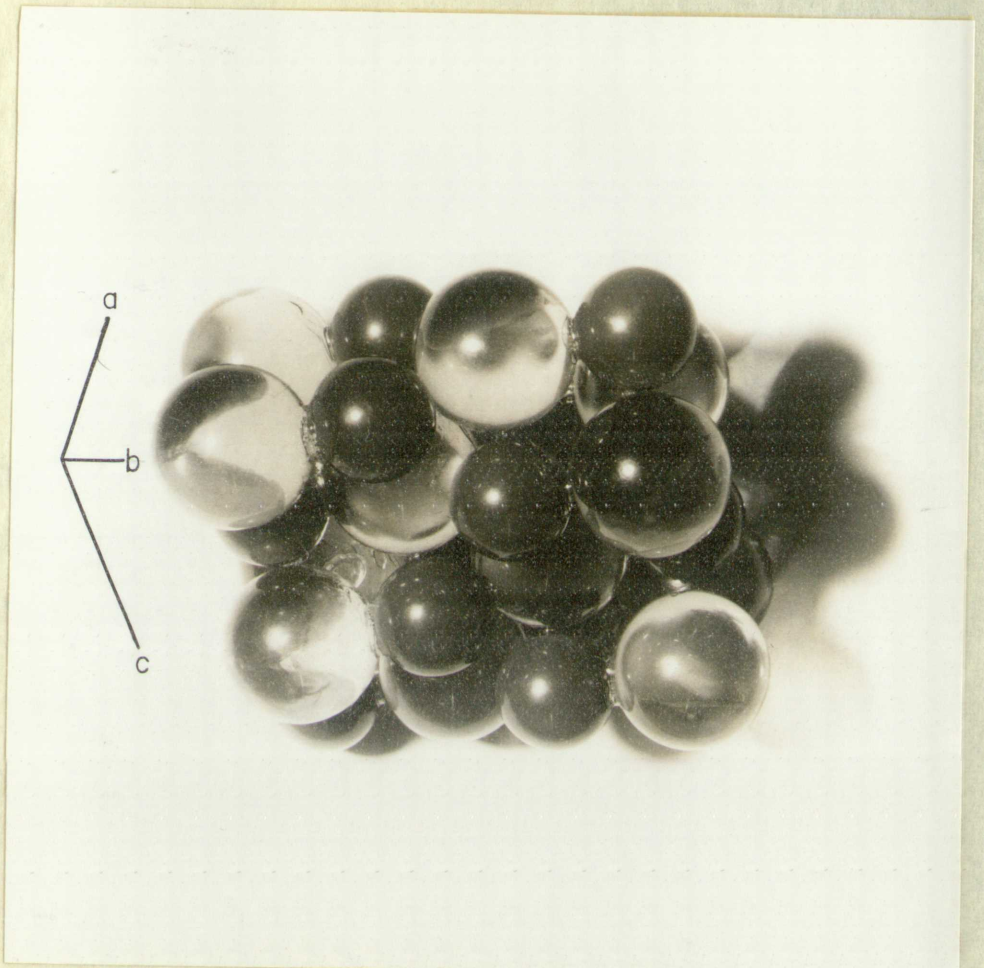


FIGURE 6 - PHOTOGRAPH OF A CRYSTAL MODEL OF CeNi. TWO CELLS ARE SHOWN.

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.

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