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ABSTRACT

We report time-of-flight neutron powder diffraction measurements which give the first direct evidence that NiF_2 undergoes a pressure induced, continuous strain transition from a tetragonal $P4_2/mnm$ (rutile) to an orthorhombic Pnnm structure at 1.83 ± 0.1 GPa. Lattice, structural and thermal parameters have been determined at pressures to 3.24 GPa. Even though the orthorhombic strain is sufficiently small that doublets are not resolved, the use of profile refinement of the diffraction spectra allows us to accurately determine the lattice parameters near the transition and to show that $(b - a)^2$ versus pressure is a straight line with slope 2.27×10^{-3} Å^2/GPa going to zero at the transition pressure. The measured atomic positions and anisotropic thermal displacements show that motion of the F atoms is responsible for the transition. All of our findings are consistent with a second order transition involving the softening of a transverse acoustic phonon mode propagating along <110> and polarized along $<1\bar{1}0>$.

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INTRODUCTION

At zero pressure, NiF_2 has the well known rutile (TiO_2) structure which belongs to the tetragonal $P4_2/mnm$ space group (No. 136). This structure may be viewed as consisting of sheets of linear F-Ni-F molecules oriented along <110> in the sheet at z = 0 and along <1$\bar{1}$0> in the sheet at z = 1/2 (Fig.7). Compounds with this rutile structure have received considerable attention as candidates for pressure induced phase transitions resulting from a softening of the acoustic mode corresponding to the effective elastic consant $\frac{1}{2}(C_{11} - C_{12})$.[1,2,3] However, before the present structural measurements on NiF_2, the second order strain transition in TeO_2, which has a slightly distorted rutile structure, was the only such transition where the relevant structural parameters, elastic constants, and acoustic phonon modes had been studied in detail at high pressure and compared with Landau's theory.[4-8]

Recent high pressure elastic constant measurements on NiF_2 by Wu[9] have shown that $\frac{1}{2}(C_{11} - C_{12})$ decreases with increasing pressure to 1.0 GPa, suggesting the possibility of a phase transition at some higher pressure. Subsequent x-ray measurements by Jamieson and Wu[10] confirmed that a tetragonal to orthorhombic transition does occur at elevated pressures. However, they found the orthorhombic strain to be sufficiently small that doublets were resolved only above 4.0 GPa. It was impossible for them to unambiguously determine the space group of the high pressure phase, to measure the true transition pressure, or to conclude whether the transition was continuous.

Using time-of-flight neutron diffraction, we have now shown that the transition is continuous and occurs at 1.83 ± 0.1 GPa and that the high pressure phase is orthorhombic Pnnm, which is a subgroup of $P4_2/mnm$ and consistent with a second order strain transition involving a soft transverse acoustic phonon mode propagating along <110> and polarized along <1$\bar{1}$0>.[11,12]

EXPERIMENTAL

The neutron measurements were performed on the time-of-flight powder diffractometer located at beam hole H-8 of Argonne's CP-5 research reactor. The configuration of this instrument is shown in Fig. 1. A polychromatic beam of neutrons from the reactor is chopped into short pulses, scattered from the sample, and detected at a scattering angle of $2\theta = 90°$ in a time focussed array of BF_3 counters. Time focussing allows the use of a comparatively large detector array with no loss of resolution.[13] The fixed 90° scattering angle makes it possible to completely eliminate reflections from the pressure cell using simple collimators in the incident and scattered beams. The diffractometer has a total flight path of 3.7 m. At the chopper speed used for this experiment, the resolution $\Delta d/d$ (FWHM) varies from 1.3% for d-spacings of 0.9 Å to 0.9% at 2.0 Å. Data were collected for about 48 hours at each pressure.

The pressure cell is a piston-cylinder device consisting of a sintered Al_2O_3 cylinder supported radially in a steel binding ring.[14] The NiF_2 powder was loaded along with deuterated methanol into a 0.69 cm o.d. x 5.1 cm long teflon tube sealed with an unsupported area type cap. The incident and scattered neutrons pass through 0.32 cm wide x 3.18 cm long slits in the steel binding ring. Although we typically use an internal CsCl pressure calibrant in our high pressure diffraction runs, the pressure calibration for this experiment is based on a separate set of CsCl measurements using identical sample geometries. This approach was taken because some CsCl reflections happened to fall at spacings of special interest in the NiF_2 pattern. Thus, the overall pressure uncertainties are estimated to be ± 0.1 GPa. Decker's equation of state[15] was used to determine pressures from the measured CsCl lattice parameters. Data were taken at nine different pressures from 0.12 to 3.24 GPa.

Lattice and structural parameters were obtained from the time-of-flight diffraction data using a profile refinement technique.[16] In this method, a calculated profile is compared to the raw data and the difference is minimized by varying the lattice, atomic position, and thermal vibration parameters. If the resolution function of the instrument is well characterized, line positions can be determined far more accurately than might be expected based on their widths, and line broadening resulting from a small strain can easily be detected and analyzed.

The small strain associated with the transition in NiF_2 offers an excellent example of the power of the profile refinement technique. Profile refinement fits at three different pressures are shown in Figs. 2, 3, and 4. Figure 2 shows the fit obtained for data at 1.37 GPa using the correct tetragonal $P4_2/mnm$ space group. Figure 3 illustrates the problems encountered if the same tetragonal space group is used to fit data above the transition at 2.87 GPa. Most notably, the (211) reflection is broadened, the (301) (112) combination appears broadened and displaced toward longer d-spacings, and the intensity of (002) is larger than calculated. (The (210) is also significantly broadened, but is hard to distinguish in this figure.) A perhaps more subtle, but equally important, problem is that several peaks appear displaced slightly either above or below their expected positions based on tetragonal symmetry. Figure 4 shows the much improved fit obtained when the same 2.87 GPa data are refined using the orthorhombic Pnnm space group. The (211) (121) doublet matches the observed width, as does the (301) (031) (112) combination. Numerous other improvements are clearly visible in the remainder of the pattern.

The profile refinements in the tetragonal phase were based on 35 allowed reflections with d-spacings between 0.88 Å and 2.34 Å; in the orthorhombic phase 59 reflections were included. For both structures the inclusion of anisotropic thermal parameters gave a small but noticeable improvement in the fits. The refined parameters at the nine different pressures studied are listed in Table I.

RESULTS

From the observed diffraction spectra in the high pressure phase, it was obvious that the structure is orthorhombic with no change in unit cell size because all lines could be indexed with a slightly distorted tetragonal cell. Since the orthorhombic lattice parameters indicate a continuous transition, the orthorhombic space group must be a subgroup of $P4_2/mnm$. The only orthorhombic subgroups obeying the observed selection rules and having the same unit cell size are Pnnm and Pnn2. When refinements using Pnn2 were attempted, the atomic positions always converged to values consistent with Pnnm symmetry, thus indicating that Pnnm is the correct space group.

The measured lattice parameters and unit cell volume versus pressure are shown in Figs. 5 and 6. The primary feature is the splitting of the tetragonal a lattice parameter into the unequal a and b orthorhombic lattice parameters beginning at about 1.83 GPa and increasing smoothly to the highest pressure studied. It is also evident that within the limits of our accuracy $(a + b)/2$, c, and the unit cell volume are all continuous through the transition, while the pressure derivatives of these quantities all change at the transition.

As discussed by Nye[17] an expansion of the elastic energy density in terms of the appropriate order parameters and elastic constants would proceed the same as has been previously done by several authors for TeO_2.[4,6,7,18] (TeO_2 belongs to space group $P4_12_12$.) The primary order parameter for the NiF_2 transition is the strain $(b - a)$. Figure 5 shows that $(b - a)^2$ versus pressure is a straight line with a slope of 2.27×10^{-3} Å^2/GPa extrapolating to zero at the transition pressure as predicted by theory. The previous treatments have also shown that when terms of sufficiently high order are retained in the expansion, the observed anomalies in the pressure derivatives of $(a + b)/2$, c, and V are also predicted.

The atomic motions associated with the transition can be easily understood by referring to Fig. 7. In a given x-y plane the Ni and F atoms lie along the <110> direction in (x,x,o) positions in the low pressure (rutile) phase. Upon going through the transition, the F atoms move in the directions shown by the arrows to (x,y,o) positions and the b axis becomes longer than a. From the measured atomic position parameters (Table I) the displacement of the F atoms is calculated to be about 0.06 Å. The data seem to indicate that the F atoms move this distance rather abruptly at the transition and then continue to move an additional small amount determined solely by the lattice strain as pressure is increased above the transition. Atomic position data for TeO_2 showed somewhat the same behavior.[4] This abrupt displacement is, however, not surprising when we consider the dimensions and orientation of the thermal ellipsoid for the F atoms. Transforming the anisotropic thermal parameters for F (Table I) to the correct principle axes, we find that the average rms thermal vibration in the tetragonal phase is about 0.16 Å in the $<1\bar{1}0>$ direction and roughly 0.07 Å or less in the other two orthogonal directions. Thus, the measured atomic displacement of 0.06 Å at the transition is only about 1/3 as large as the rms thermal displacement in the same direction. It is also significant to note that the observed direction of largest thermal displacement is consistent with the transition mechanism. This is the first case where high pressure measurements of anisotropic thermal parameters have indicated the displacement pattern involved in a continuous phase transition.

DISCUSSION

We have shown that NiF_2 undergoes a continuous pressure induced tetragonal to orthorhombic phase transition at 1.83 ± 0.1 GPa. The high pressure space group has been shown to be Pnnm which is consistent with the transition being second order with the strain being the primary order parameter.[11,12] It is relevant to note that Austin[19] has demonstrated that an orthorhombic polymorph of NiF_2 can be produced by quenching from nonhydrostatic high pressures, presumably being stabilized by residual stresses.[20] Our measurements confirm the suggestion by Nagel and O'Keefe[20] that this orthorhombic form of NiF_2 has the $CaCl_2$ structure. However, diffraction spectra taken after our hydrostatic pressure measurements confirmed that our sample had returned completely to the rutile structure.

It is suspected that the transition is driven by a soft transverse acoustic phonon mode propagating along <110> and polarized along $<1\bar{1}0>$; however, this has not yet been confirmed experimentally. The effective elastic constant corresponding to this mode, $\frac{1}{2}(C_{11} - C_{12})$ has been shown to soften upon increasing pressure to 1.0 GPa, but has not been measured up to the transition pressure. The observed atomic motions associated with the transition are identical to those of the B1g (Γ_3^+) optic mode at zero wave vector,[21] leading us to speculate that this optic modes may also play a role in the transition.

NOTATION

a,b,c = lattice parameters
C_{ij} = elastic constants
d = plane spacing
h,k,l = Miller indices
P = pressure
U_{ij} = elements of the thermal displacement tensor
V = unit cell volume
x,y,z = atomic positions
θ = Bragg angle

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Table I. Structural and thermal parameters of NiF_2 versus pressure. (Numbers in parenthesis are statistical uncertainties of last significant figures.)

(a) Lattice parameters and atomic positions

P(GPa)	a(Å)	b(å)	c(Å)	x	y
0.12	4.6499(3)		3.0836(3)	0.3040(4)	
0.65	4.6404(3)		3.0801(3)	0.3031(4)	
1.00	4.6348(3)		3.0783(3)	0.3037(4)	
1.37	4.6293(3)		3.0760(3)	0.3031(4)	
1.75	4.6244(3)		3.0735(3)	0.3029(4)	
2.12	4.6063(8)	4.6331(8)	3.0717(3)	0.294(2)	0.312(2)
2.49	4.5967(8)	4.6358(6)	3.0716(3)	0.296(1)	0.310(1)
2.87	4.5884(7)	4.6376(6)	3.0708(4)	0.293(1)	0.311(1)
3.24	4.5808(8)	4.6386(7)	3.0698(4)	0.293(1)	0.312(1)

(b) Thermal parameters (x 10^3, $Å^2$) defined such that the temperature factor takes the form:

$$\exp[-2\pi^2(\frac{U_{11}h^2}{a^2} + \frac{U_{22}k^2}{b^2} + \frac{U_{33}l^2}{c^2} + \frac{2\ U_{12}h\,k}{a\,b})]$$

	Ni				F			
P(GPa)	U_{11}	U_{22}	U_{33}	U_{12}	U_{11}	U_{22}	U_{33}	U_{12}
0.12	3(1)		1(1)	-5(1)	11(1)		6(2)	-15(2)
0.65	4(1)		1(1)	-4(1)	12(1)		4(2)	-13(2)
1.00	5(1)		0(1)	-3(1)	12(1)		5(2)	-12(1)
1.37	5(1)		-1(1)	-2(1)	13(1)		4(2)	-12(1)
1.75	6(1)		-1(1)	-1(1)	14(1)		2(2)	-12(2)
2.12	8(3)	4(2)	2(1)	-1(1)	12(4)	17(4)	2(2)	-10(2)
2.49	18(3)	-4(2)	2(1)	-1(1)	24(4)	30(3)	1(2)	-12(2)
2.87	18(3)	-6(2)	1(1)	-1(2)	29(4)	-1(2)	-1(2)	-11(2)
3.24	20(3)	-6(2)	1(1)	-3(2)	30(4)	0(3)	2(2)	-12(2)

FIGURE CAPTIONS

Fig. 1 Schematic drawing of high pressure time-of-flight powder diffractometer located at the H-8 beam hole of Argonne's CP-5 research reactor.

Fig. 2 Refinement profile of NiF_2 diffraction data at 1.37 GPa. Plus marks are the raw data points. The solid line is the calculated profile. Background has been removed before plotting. Tick marks below the profile indicate positions of allowed reflections. A few reflections are indexed in parentheses above the profile.

Fig. 3 Refinement profile of NiF_2 diffraction data at 2.87 GPa using the incorrect $P4_2/mnm$ space group. (Format is the same as Fig. 2.) Note especially the poor fitting of the (211), (002), (112), and (301) reflections.

Fig. 4 Refinement profile of NiF_2 diffraction data at 2.87 GPa using the correct Pnnm space group. (Format is the same as Fig. 2.)

Fig. 5 Lattice parameters a and b of NiF_2 versus pressure showing the splitting of the tetragonal a into the orthorhombic a and b. The lower curve shows the square of the strain, (b - a), versus pressure. Standard deviations are smaller than the points.

Fig. 6 Lattice parameter c and unit cell volume of NiF_2 versus pressure. Standard deviations are smaller than the points.

Fig. 7 Projection of the NiF_2 structure onto the x-y plane. Open circles indicate atoms at $z = 0$; shaded circles indicate $z = 1/2$. Arrows on the F atoms indicate the atomic motions associated with the transition. In the tetragonal phase $a = b$ and the F atoms lie at (x,x,o); in the orthorhombic phase $b > a$ and the F atoms lie at (x,y,o) with $y > x$.

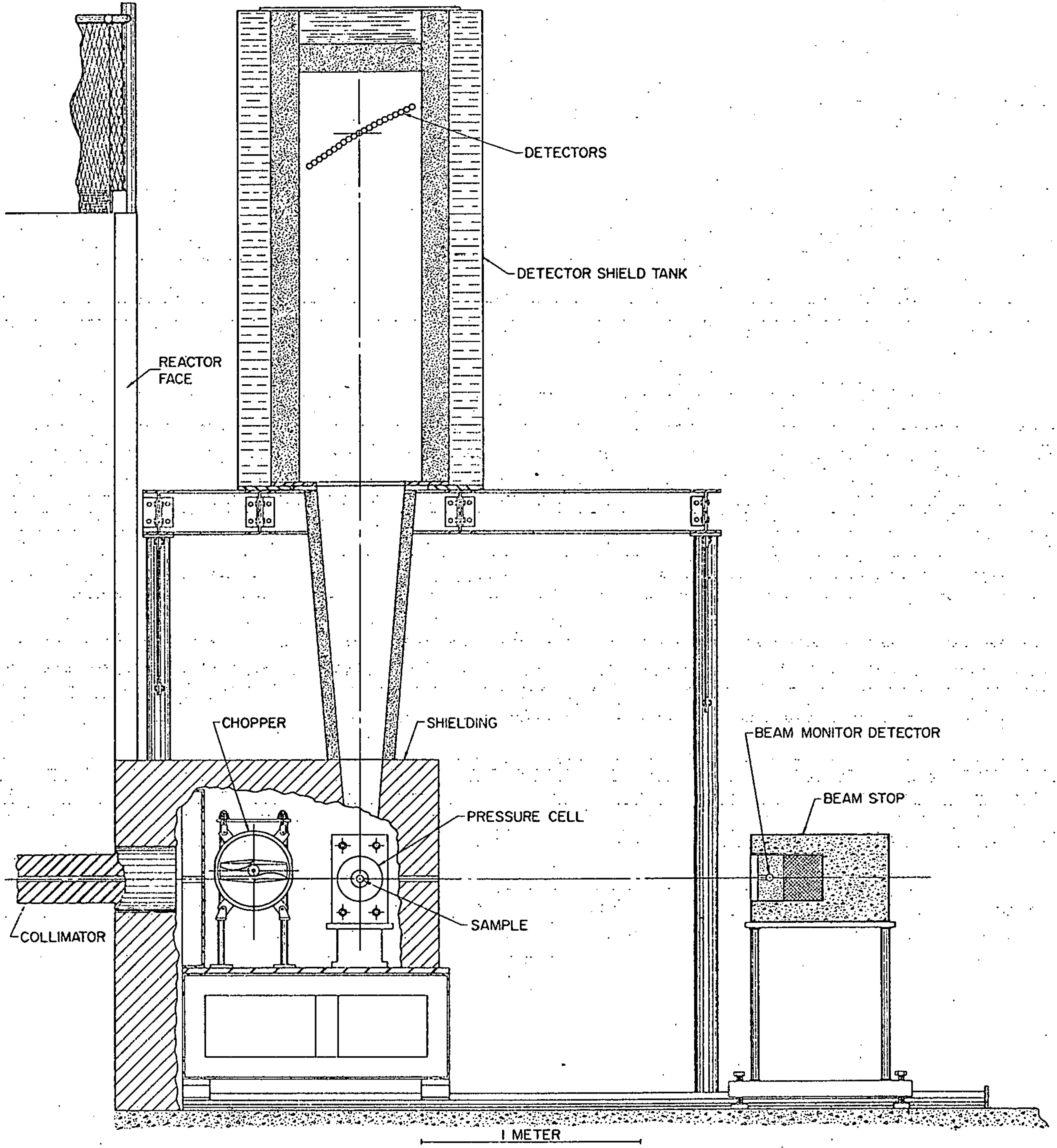

DETECTORS
DETECTOR SHIELD TANK
REACTOR FACE
CHOPPER
SHIELDING
BEAM MONITOR DETECTOR
BEAM STOP
PRESSURE CELL
COLLIMATOR
SAMPLE
I METER

Fig 1

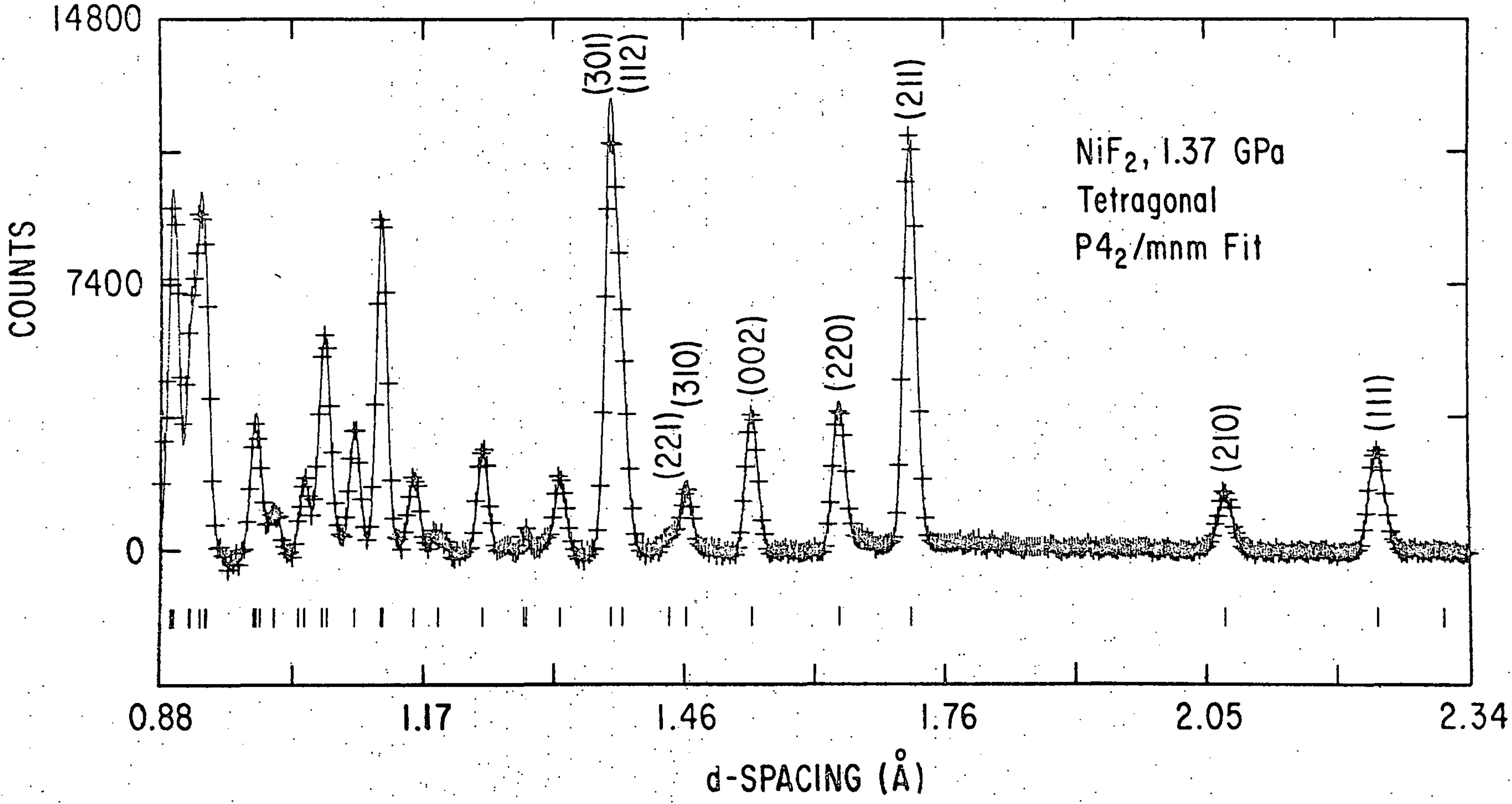
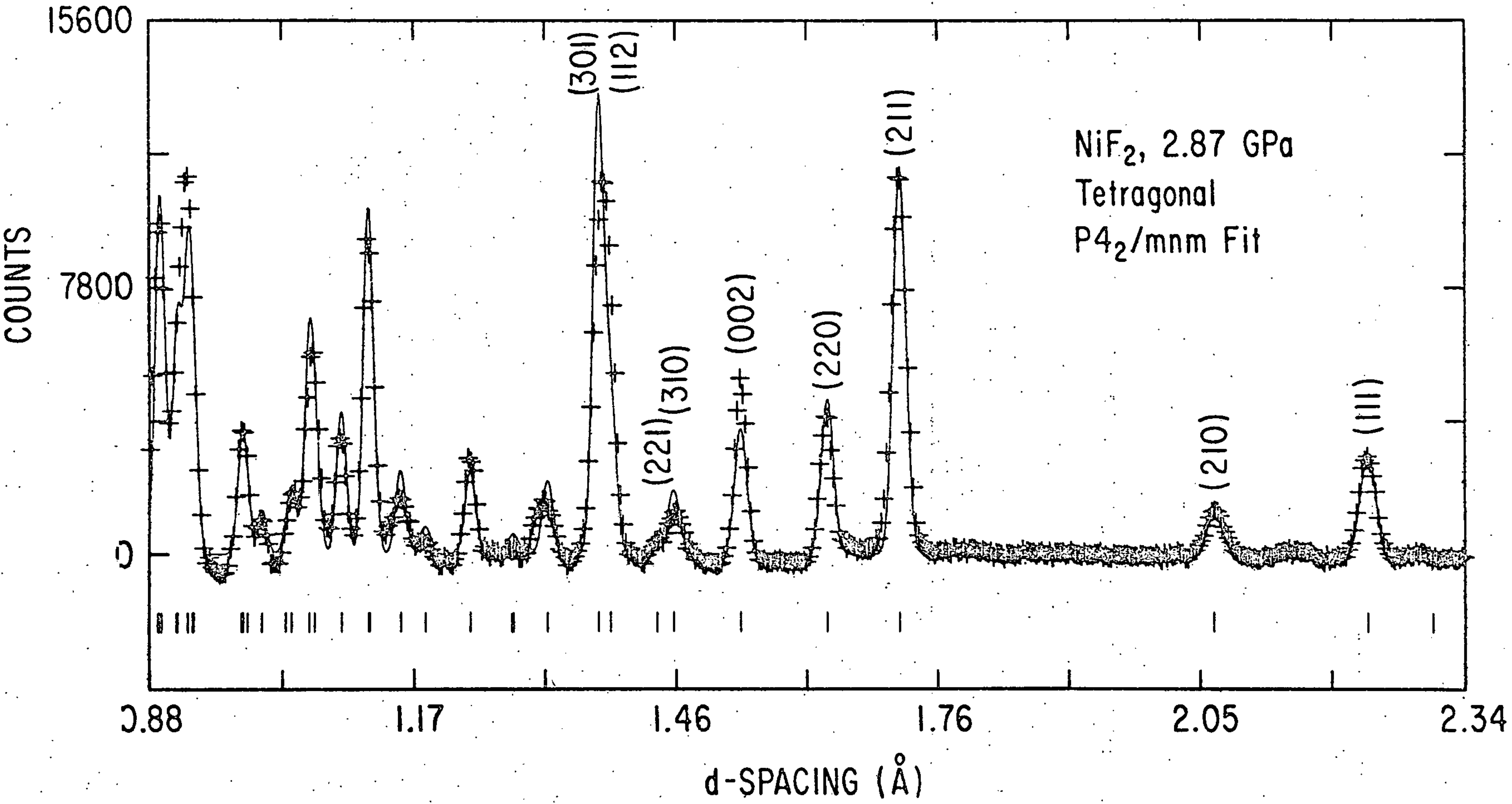

14800
7400
0
COUNTS
0.88
1.17
1.46
1.76
2.05
2.34
d-SPACING (Å)
(301)
(112)
(221)
(310)
(002)
(220)
(211)
(210)
(111)
NiF$_2$, 1.37 GPa
Tetragonal
P4$_2$/mnm Fit

Fig 2



NiF$_2$, 2.87 GPa
Tetragonal
P4$_2$/mnm Fit
COUNTS
15600
7800
0
(301)
(112)
(221)
(310)
(002)
(220)
(211)
(210)
(111)
0.88
1.17
1.46
1.76
2.05
2.34
d-SPACING (Å)

Fig 3

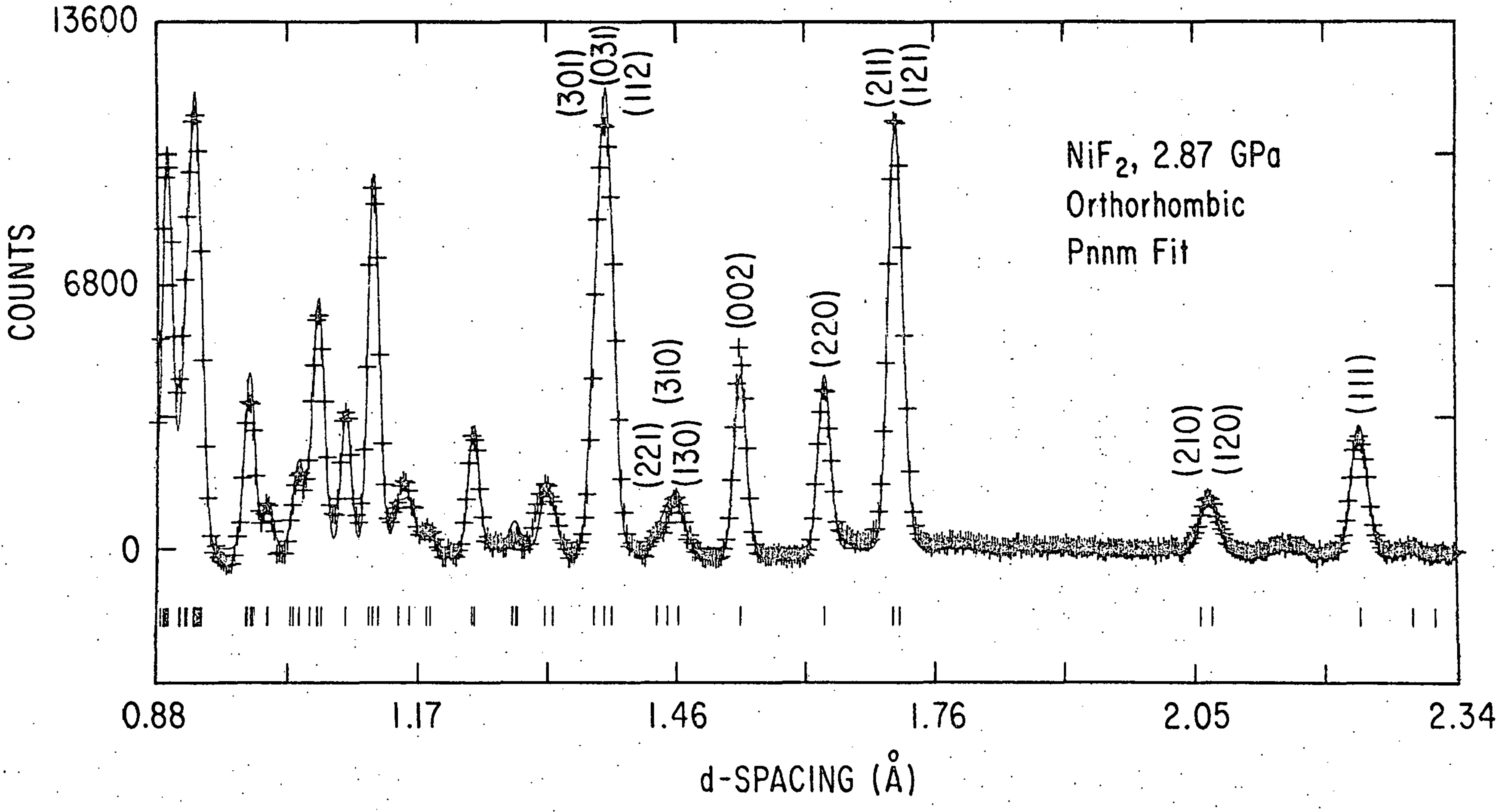

NiF$_2$, 2.87 GPa
Orthorhombic
Pnnm Fit
COUNTS
13600
6800
0
d-SPACING (Å)
0.88
1.17
1.46
1.76
2.05
2.34
(301)
(031)
(112)
(221)
(310)
(130)
(002)
(220)
(211)
(121)
(210)
(120)
(111)

Fig 4

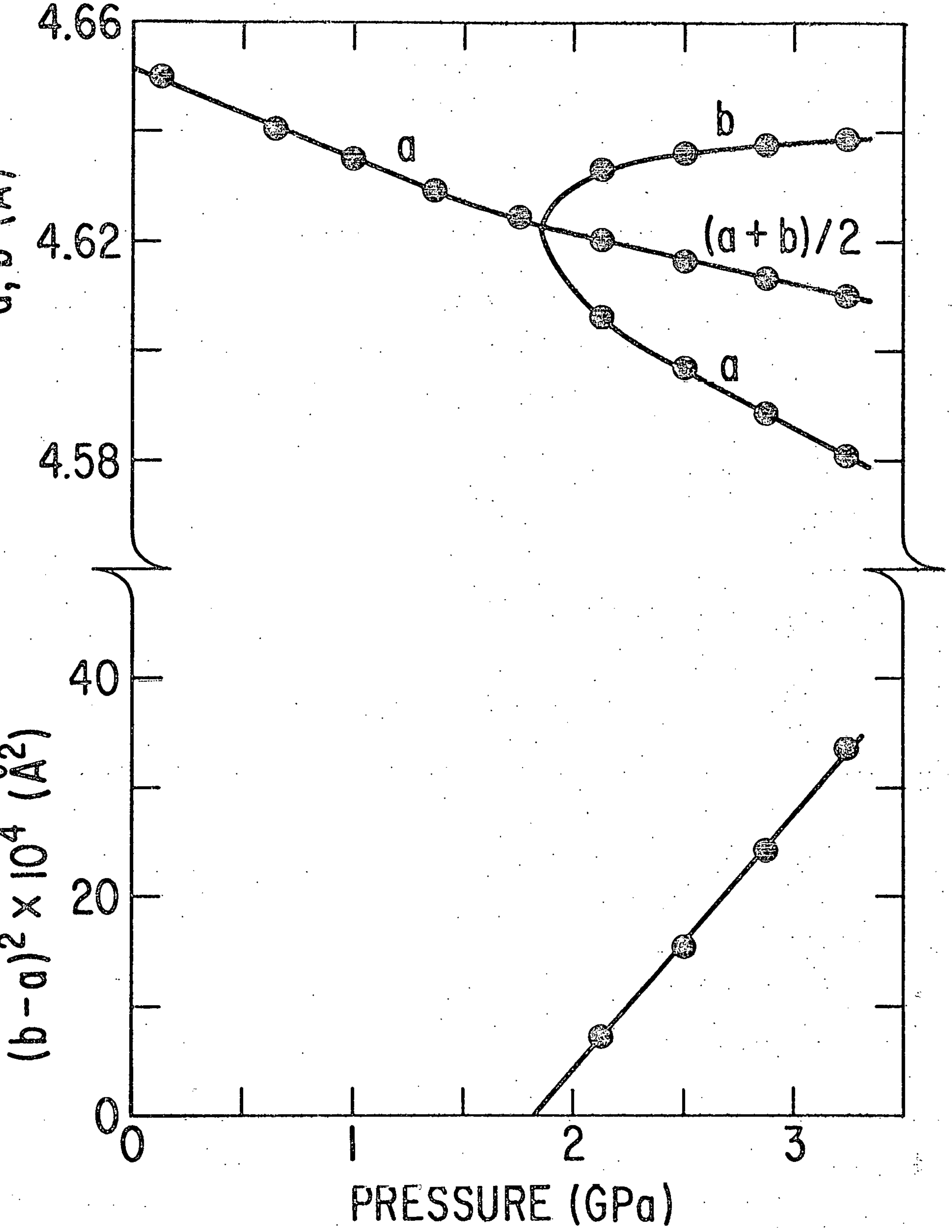

4.66
4.62
4.58
a, b (Å)
a
b
(a + b)/2
a
40
20
0
$(b-a)^2 \times 10^4$ (Å^2)
0
1
2
3
PRESSURE (GPa)

Fig 5

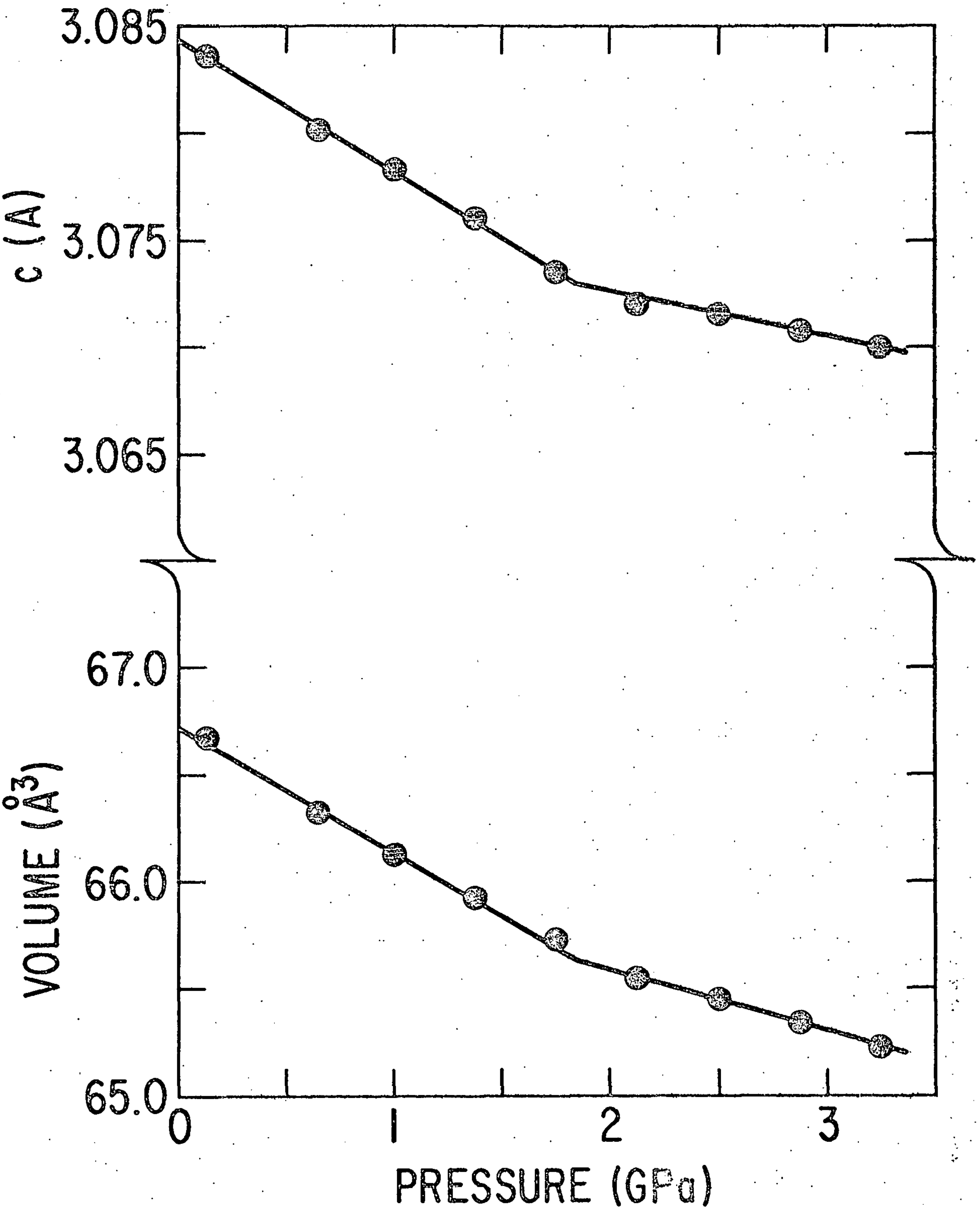


Fig 6

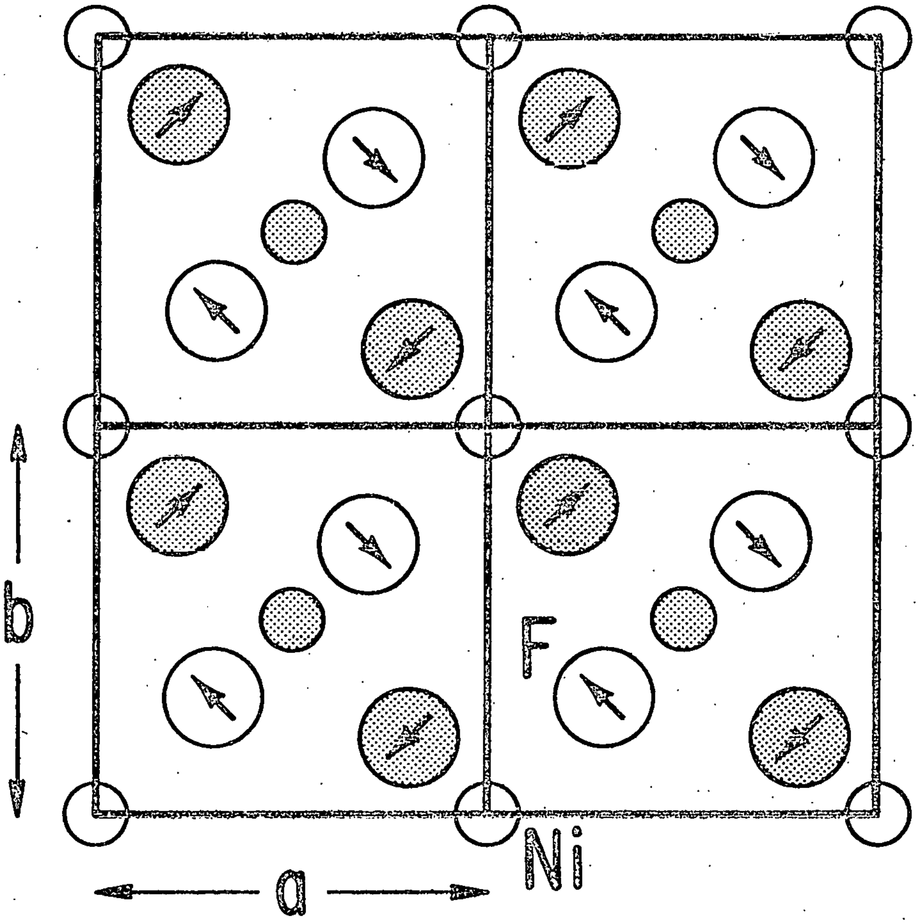


Fig 7