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Pressure-induced strain transition in NiF_2

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We report time-of-flight neutron powder diffraction measurements which give the first direct evidence that NiF_2 undergoes a pressure-induced continuous phase transition from tetragonal $P4_2/mnm$ (rutile) to orthorhombic *Pnnm* at 18.3 ± 1 kbar. The square of the strain $(b-a)$ varies linearly with pressure above the transition and extrapolates to zero at the transition pressure. Measured atomic positions and thermal displacements show that motion of the F atoms is responsible for the transition.

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 $\langle 110\rangle$ in the sheet at $z=0$ and along $\langle 1\bar{1}0\rangle$ in the sheet at $z=\frac{1}{2}$ (Fig. 3). Compounds with this rutile structure have received considerable attention as candidates for pressure-induced phase transitions resulting from a softening of the acoustical mode corresponding to the effective elastic constant $\frac{1}{2}(C_{11}-C_{12})$.[1-3] 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 details of the transition mechanism have been established by measuring the relevant structural parameters, elastic constants, and acoustical-phonon modes at high pressure.[4-7]

Recent high-pressure elastic constant measurements on NiF_2 by Wu[8] have shown that $\frac{1}{2}(C_{11}-C_{12})$ decreases about 11% upon increasing pressure to 10 kbar, suggesting the possibility of a phase transition at some higher pressure. Subsequent x-ray measurements by Jamieson and Wu[9] 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 40 kbar. 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 18.3 ± 1 kbar and that the high-pressure phase is orthorhombic *Pnnm*, which is a subgroup of $P4_2/mnm$. This is consistent with a second-order strain transition resulting from a softening of the transverse acoustical-phonon mode which propagates along $\langle 110\rangle$ and corresponds to the effective elastic constant $\frac{1}{2}(C_{11}-C_{12})$.[10,11]

The neutron measurements were performed on the H-8 time-of-flight powder diffractometer at Argonne's CP-5 research reactor. Measurements were made under hydrostatic conditions at nine different pressures from 1.2 to 32.4 kbar using the pressure cell described previously.[4] The pressure calibration is based on a separate set of CsCl measurements; thus, uncertainties are estimated to be ±1 kbar. The NiF_2 diffraction data were analyzed using a profile-refinement technique[12] based on all allowed reflections with *d* spacings between 0.88 and 2.34 Å. Using this procedure, lattice, atomic position, and anisotropic thermal parameters were determined at each of the pressures studied.

As pressure was increased, the onset of the transition was evidenced in the raw diffraction data by a gradual asymmetric broadening of some tetragonal lines coupled with a slight displacement of some lines from their correct tetragonal positions. Since either orthorhombic or monoclinic structures can be produced by a continuous distortion from a tetragonal space group, refinements were attempted for both of these symmetries. It was confirmed that the high-pressure phase is orthorhombic, as had previously been concluded by Jamieson and Wu.[9] Selection rules in the high-pressure phase showed that the unit cell size did not change at the transition. Since the orthorhombic lattice parameters indicated 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 *Pnn*2. Profile refinements based on *Pnnm* consistently gave good fits to the data in the high-pressure phase. When refinements using *Pnn*2 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. 1 and 2. The primary feature is the splitting of the tetragonal *a* lattice parameter into the unequal *a* and *b* orthorhomibc lattice parameters beginning at about 18.3 kbar and increasing smoothly to the highest pressure studied. It is also evident that within the limits of our accuracy $\frac{1}{2}(a+b)$, 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[13] 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.[4,6,7,14] (TeO_2 belongs to space group $P4_12_12$.) The primary order parameter for the NiF_2 transition is the strain $(b-a)$. Figure 1 shows that $(b-a)^2$ versus pressure is a straight line with a slope of 2.27×10^{-4} Å^2/kbar 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 $\frac{1}{2}(a+b)$, c, and V are also predicted.

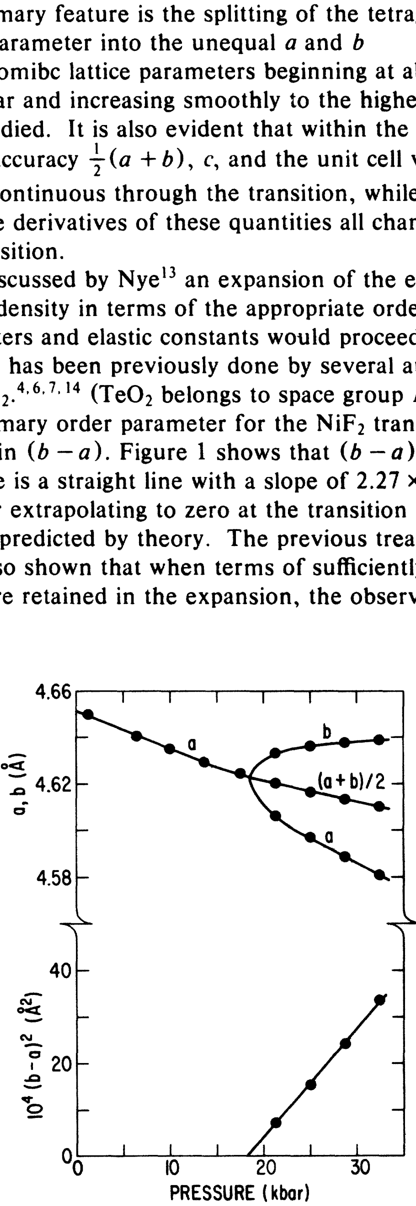

FIG. 1. Lattice parameters *a* and *b* of NiF_2 vs pressure showing the splitting of the tetragonal *a* into the orthorhombic *a* and *b*. The lower curve shows the square of the strain $b-a$ versus pressure. Standard deviations are smaller than the points.

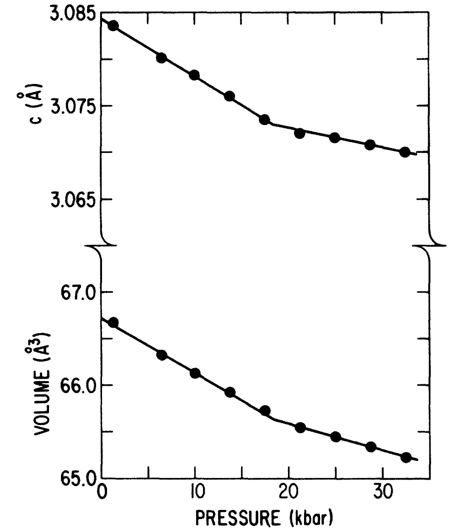

FIG. 2. Lattice parameter *c* and unit cell volume of NiF_2 vs pressure. Standard deviations are smaller than the points.

The atomic motions associated with the transition can be easily understood by referring to Fig. 3. In a given *x-y* plane the Ni and F atoms lie along the ⟨110⟩ direction in $(x,x,0)$ positions in the low-pressure (rutile) phase. Upon going through the transition, the F atoms move in the directions shown by the arrows to $(x,y,0)$ positions and the *b* axis becomes longer than *a*. The measured value of *x* in the tetragonal phase varies slightly from 0.3040(4) at 1.2 kbar to 0.3029(4) at 17.5 kbar. In the orthorhombic phase $x=0.294(2)$ and $y=0.311(2)$, and neither varies with pressure within the uncertainties. From these atomic position parameters the displacement of the F atoms is calculated to be 0.06(1) 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 change in the equilibrium atomic position is, however, not surprising when we consider the dimensions and orientation of the thermal ellipsoid for the F atoms. Transforming the measured anisotropic thermal parameters for F to the correct principle axes, we find that the average rms thermal vibration in the tetragonal phase is 0.16(2) Å in the $\langle 1\bar{1}0\rangle$ direction and 0.07(2) Å or less in the other two orthogonal directions. Thus, the measured atomic displacement of 0.06 Å at the transition is only about $\frac{1}{3}$ 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

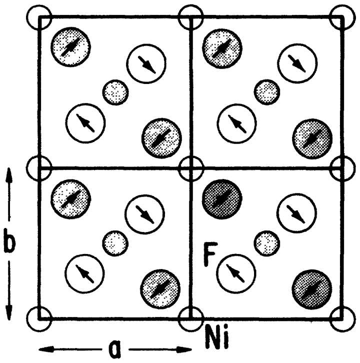

FIG. 3. Projection of the NiF_2 structure onto the x-y plane. Open circles indicate atoms at $z=0$; shaded circles indicate $z=\frac{1}{2}$. Arrows on the F atoms indicate the atomic motions associated with the transition. In the tetragonal phase $a=b$ and the F atoms lie at $(x,x,0)$; in the orthorhombic phase $b>a$ and the F atoms lie at $(x,y,0)$ with $y>x$.

is perfectly consistent with the transition mechanism. This is the first case where high-pressure measurements of anisotropic thermal parameters have been used to help establish the displacement pattern involved in a continuous phase transition.

In conclusion, we have shown that NiF_2 undergoes a continuous pressure-induced tetragonal-to-orthorhombic phase transition at 18.3±1 kbar. 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.[10,11] It is relevant to note that Austin[15] has demonstrated that an orthorhombic polymorph of NiF_2 can be produced by quenching from nonhydrostatic high pressures, presumably being stabilized by residual stresses.[16] Our findings confirm the suggestion by Nagel and O'Keefe[16] that this orthorhombic phase 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-acoustical-phonon mode propagating along $\langle 110\rangle$ and polarized along $\langle 1\bar{1}0\rangle$; 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 10 kbar, but has not been measured up to the transition pressure. The observed atomic motions associated with the transition are identical to those of the $B_{1g}(\Gamma_3^+)$ optical mode at zero wave vector,[17] leading us to speculate that this optical mode may also play a role in the transition.

Note added in proof. Dr. I. J. Fritz (Sandia Laboratory) has recently made a preliminary measurement of the $\frac{1}{2}(C_{11}-C_{12})$ elastic constant in NiF_2 to 23 kbar, at which point the sample broke. He observed continued softening of the elastic constant, but no evidence for the transition.

ACKNOWLEDGMENT

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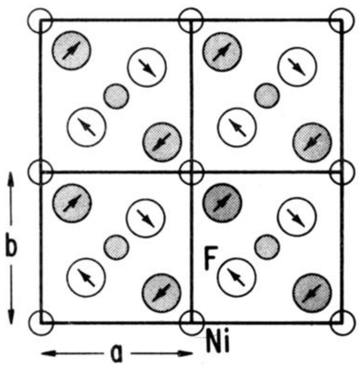

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