

improves the accuracy of strong low-order structure factors which are important for deformation electron-density studies. To provide high-precision measurements of the weaker structure factors an intense X-ray source, such as synchrotron radiation, is then desirable.

We acknowledge Dr Dudley Creagh here for his calculations of absorption coefficients and dispersion corrections. This work was supported by the Australian Research Council.

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Acta Cryst. (1993). **B49**, 984–987

Single-Crystal Pulsed Neutron Diffraction from NiF₂ and FeF₂: the Effect of Magnetic Order on the Fluorine Positions

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(Received 9 March 1993; accepted 9 July 1993)

Abstract

Extended single-crystal data sets have been collected by means of pulsed neutron diffraction from NiF₂ at 295, 80 and 15 K, and from FeF₂ at 295 and 15 K to examine the effect of magnetic order on the fluorine nuclear positions. A predicted internal displacement has been validated in NiF₂, whereas in FeF₂ it could not be established unambiguously. The positional parameters are compared with those obtained from γ -ray diffraction data, recorded from the same samples. In view of the excellent agreement there is no evidence for any polarization effects in the anti-ferromagnetic phase.

1. Introduction

It has been predicted that the magnetic ordering in transition-metal difluorides is accompanied by small internal magnetostrictive shifts of the anions (Jauch, 1991). In MnF₂ such a shift has been established by extended γ -ray and neutron diffraction studies. In the magnetically ordered phase, however, the two methods did not yield identical results for the fluorine positional parameter (Jauch, McIntyre & Schultz, 1990). The significant difference can be attributed to a polarization of the fluorine core electron density (Jauch & Stewart, 1991). In the absence of neutron diffraction data this impact of magnetic

order on the charge density would have gone unnoticed.

NiF₂ and FeF₂, like the other transition-metal difluorides, exhibit a rutile-type structure (space group $P4_2/mnm$). They undergo an antiferromagnetic phase transition near 70 K. The present neutron study therefore has a twofold objective: (i) an experimental test of the predicted temperature variation of the fluorine x parameter and (ii) an accurate determination of the mean thermal nuclear positions to test whether a polarization of the F atoms is typical for this class of antiferromagnets. The results are compared with those obtained from γ -ray diffraction data, collected from the same samples (Palmer & Jauch, 1993).

2. Crystal data

FeF₂ orders antiferromagnetically at 78 K with the opposing moments aligned along c ; the structure remains tetragonal. The lattice constants are $a = 4.6974$, $c = 3.3082$ Å at room temperature (RT) and $a = 4.6933$, $c = 3.3007$ Å at 15 K (LT) (Haefner, 1964). The single-crystal specimen was a prism with a volume of 9.4 mm³.

In NiF₂ ($T_N = 73$ K) the magnetic moments are aligned perpendicular to the c axis and form a slightly canted antiferromagnetic structure which lowers the symmetry to orthorhombic. The weak ferromagnetic moment points along a , and in the absence of an external field there are four possible magnetic domains which have been made visible by highly collimated γ -rays (Palmer & Jauch, 1991). The departure from tetragonal symmetry, however, is very small. The lattice constants are $a = 4.6501$, $c = 3.0835$ Å at RT, $a = 4.6463$, $c = 3.0781$ Å at 80 K and $a = 4.6484$, $b = 4.6472$, $c = 3.0745$ Å at LT (Haefner, Stout & Barrett, 1966). The sample was a parallelepiped with dimensions $3.3 \times 2.8 \times 1.5$ mm.

3. Experimental

Diffraction data were obtained by the time-of-flight Laue technique using the single-crystal instrument at the Argonne pulsed spallation neutron source IPNS. Both specimens were investigated at RT and LT; an additional data set from NiF₂ was collected at 80 K. For NiF₂, the temperature was checked by monitoring the temperature dependence of the magnetic reflection (001).

After LT data had been collected from NiF₂ in the twinned state, it turned out that refinements of the corresponding γ -ray diffraction data failed to converge to acceptably low statistical indicators. In order to exclude any disturbing influence of twinning on the results, LT data have been recollected from a single domain crystal. Here, the sample was mounted

Table 1. *Data-collection conditions*

	I*	II†
λ range (Å)	0.5–3.0	0.4–2.4
$(\sin\theta/\lambda)_{\max}$ (Å ⁻¹)	1.6	2.0
No. of reflections per histogram	~60	~150
Counting time per histogram (h)	3	5
Accelerator beam target	Enriched	Depleted ²³⁵ U

* I: NiF₂ at room temperature (RT), 80 K (2 h) and low temperature (LT) (multidomain).

† II: NiF₂ at LT (single domain) and FeF₂ at RT and LT.

between two CoSm permanent magnets generating a field of about 200 Oe along the a direction. It has been verified in a preceding γ -ray experiment that this field strength is sufficient to keep the crystal a single domain.

Essential data collection conditions are summarized in Table 1. The Laue spots from NiF₂ were integrated over a box of $5 \times 5 \times 5$ elements of the three-dimensional data array (histogram). For the somewhat broadened peaks from FeF₂ the ellipsoidal $\sigma(I)/I$ integration technique (Wilkinson, 1986) was applied giving considerable improvement in precision. Further details of data reduction are described in a previous paper (Jauch, Schultz & Schneider, 1988).

Absorption corrections were based either on the real crystal shape (NiF₂) or on the corresponding spherical volume (FeF₂). Effective absorption coefficients were calculated from the total cross sections: $\mu(\text{NiF}_2) = 0.80 + 0.075 \lambda(\text{Å})$, $\mu(\text{FeF}_2) = 0.54 + 0.039 \lambda(\text{Å})$, with μ in cm⁻¹. These values represent an upper limit for the contributions due to neutron capture, incoherent scattering and inelastic thermal diffuse scattering.

4. Results

Refinements based on $|F|^2$ were performed with the multiwavelength program *ANVLS* using the following scattering lengths: $b(\text{F}) = 0.5654$, $b(\text{Ni}) = 1.03$, $b(\text{Fe}) = 0.954 \times 10^{-12}$ cm (Sears, 1992). The observations were weighted according to $w = [\sigma_{\text{cs}}^2 + P^2|F|^4 + Q]^2$ with $\sigma_{\text{cs}}^2 =$ counting statistical variance, $P = 0.04$ (instrumental imprecision), $Q =$ constant. In contrast to the other contributions, Q accounts for systematic errors which are common to all data points, *e.g.* common background errors. In practice, its effect is small in comparison to the random uncertainties, as it only reduces the weights of the weakest reflections.

The LT data sets contain mixed nuclear and magnetic reflections ($h + k + l$ odd). Reflections of this type with $\sin\theta/\lambda \leq 0.7$ Å⁻¹ were excluded from the refinements.

Equally acceptable fits were obtained with both Zachariasen's (1967) extinction model (type I) and the Becker & Coppens (1974) model (type I, Lor-

Table 2. Results for NiF₂

		295 K	80 K	15 K Multidomain	15 K Single domain
Ni	U_{11} (Å ²)	0.00500 (3)	0.00217 (3)	0.00213 (3)	0.00191 (4)
	U_{33}	0.00384 (5)	0.00180 (5)	0.00162 (4)	0.00156 (4)
	U_{12}	-0.00036 (3)	-0.00013 (2)	-0.00009 (2)	-0.00014 (3)
F	U_{11}	0.00939 (5)	0.00455 (4)	0.00432 (3)	0.00411 (4)
	U_{33}	0.00615 (6)	0.00350 (6)	0.00337 (5)	0.00322 (6)
	U_{12}	-0.00428 (5)	-0.00147 (4)	-0.00130 (3)	-0.00119 (4)
x	0.30365 (4)	0.30351 (3)	0.30335 (3)	0.30332 (4)	
No. of observations	1604	1648	1646	2975	
Unique reflections	516	535	527	1000	
$R(F^2)^*$	0.054	0.058	0.045	0.072	
$R_{\text{int}}(F^2)^\dagger$	0.025	0.030	0.018	0.047	
$wR(F^2)^\ddagger$	0.072	0.075	0.068	0.108	
η_{Zach} (°arc)	8.1 (2)	14.9 (3)	23.2 (4)	14.0 (4)	
η_{obs} (°arc)	17			21	

$$* R(F^2) = \sum |F_{\text{obs}}^2 - F_{\text{calc}}^2| / \sum F_{\text{obs}}^2$$

$$^\dagger R_{\text{int}}(F^2) = \sum \sigma_{\text{cs}}(F_{\text{obs}}^2) / \sum F_{\text{obs}}^2$$

$$^\ddagger wR(F^2) = [\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2 / \sum wF_{\text{obs}}^4]^{1/2}$$

Table 3. Results for FeF₂

		295 K	15 K
Fe	U_{11} (Å ²)	0.00650 (5)	0.00214 (4)
	U_{33}	0.00553 (5)	0.00214 (4)
	U_{12}	-0.00093 (3)	-0.00019 (2)
F	U_{11}	0.01250 (7)	0.00475 (4)
	U_{33}	0.00847 (8)	0.00404 (5)
	U_{12}	-0.00623 (8)	-0.00165 (3)
x	0.30133 (5)	0.30120 (4)	
No. of observations	1977	1770	
Unique reflections	948	899	
$R(F^2)$	0.092	0.072	
$R_{\text{int}}(F^2)$	0.058	0.029	
$wR(F^2)$	0.099	0.086	
η_{Zach} (°arc)	97 (4)	69 (3)	
η_{obs} (°arc)	85	88	

entzian distribution), which is to be expected for the angular range covered by the instrument ($\theta = 30$ – 60° ; Jauch, Schultz & Schneider, 1988).

The final results are presented in Tables 2 and 3. Here, η_{Zach} denotes the Gaussian mosaic width (FWHM) in Zachariasen's theory, and η_{obs} is the mean width of γ -ray rocking curves, averaged over three perpendicular crystal orientations.

The NiF₂ data sets each contain about 600 observations (FeF₂: 20 observations) with an extinction factor $y \leq 0.8$ ($|F_{\text{obs}}|^2 = y|F_{\text{kin}}|^2$). Fixing the mosaicity to η_{obs} had no appreciable influence on the x parameters.

Although the final R values appear to be large, closer inspection shows that the contributions to R can be acceptably accounted for by the known random components. The reduced precision in individual reflections is compensated by the high degree of over-determination. No weak reflections were discarded as 'unobserved', and no threshold was applied to exclude the most severely extinction-affected reflections. Any tentative use of such thresholds had no appreciable influence on the thermal parameters. Allowance for third-order anharmonic motion of the F nuclei yielded only non-significant values.

Table 4. Results from high-order refinements of γ -ray data (Palmer & Jauch, 1993)

	$x(F)$
NiF ₂ (295 K)	0.30364 (9)
NiF ₂ (15 K)*	0.30326 (8)
FeF ₂ (10 K)	0.30121 (8)

* Single-domain sample.

A refinement of the LT NiF₂ single domain data in the orthorhombic space group $Pnmm$ gave $x = 0.30333$ (6), $y = 0.30332$ (7), and thermal parameters which remain unchanged within their standard deviations from the values in Table 2. Obviously, there is no indication that the F atoms move out of the diagonal of the ab plane.

5. Discussion

The observed change of the fluorine positional parameter $\Delta x = x(\text{RT}) - x(\text{LT}) = 3.3$ (6) $\times 10^{-4}$ in NiF₂ is in satisfactory agreement with the predicted value of 4.5×10^{-4} (Jauch, 1991). In case of FeF₂ the calculated shift amounts to only 2.3×10^{-4} , which is not readily detectable, especially in view of the unfavourable F/Fe scattering-power ratio. Whereas the sign of the experimental result is in accordance with prediction, the precision attained precludes a conclusive decision upon the magnitude.

The positional parameters derived from extended γ -ray diffraction data sets (Table 4) are in remarkably good agreement with the results of the neutron investigations. From the concurrence of the neutron and γ -ray determined values at LT, it follows that, in contrast to MnF₂, there is no evidence for a polarization of the fluorine core electrons in the magnetically ordered state in NiF₂ and in FeF₂. Presently, we can offer no explanation for this different behaviour, except to suggest that it might be related to the high symmetry of the half-filled d shell in Mn²⁺.

In NiF₂, at 80 K the F atoms have already shifted from their RT positions, which reflects the considerable amount of short-range order above the transition as has been observed, *e.g.* from birefringence measurements (Jahn, 1973).

In Table 1, conditions I and II refer to data obtained with and without, respectively, an enriched ²³⁵U 'booster' target as part of the IPNS neutron source. At the IPNS, pulses of high-energy protons bombard a target to produce neutrons by spallation. Fast fission from an enriched uranium target provided a 2.5-fold increase in neutron flux over that of a depleted uranium target. However, the proportion of delayed neutrons to prompt neutrons also increases (Epperson, Carpenter, Thiyagarajan & Heuser, 1990). The delayed neutrons appear as a

steady-state source of background which could possibly offset the gain in flux by reducing the accuracy of the intensity measurements. In the case of NiF₂, an LT data set was collected under each of the two conditions. From Table 2, it is obvious that the results are hardly affected and certainly not contaminated by the increase in the delayed neutron background.

We wish to thank Dr I. R. Jahn for the loan of the samples. The work at Argonne was supported by the Office of Basic Energy Sciences Division of Materials Sciences, US Department of Energy, under contract W-31-109-Eng-38.

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Acta Cryst. (1993). **B49**, 987–996

Multistage Diffusionless Pathways for Reconstructive Phase Transitions: Application to Binary Compounds and Calcium Carbonate

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(Received 26 May 1993; accepted 3 August 1993)

Abstract

The distinction between ‘displacive’ and ‘reconstructive’ phase transformations is subjective, but rigorous classification into three types is possible using symmetry criteria. Type I shows a group-subgroup relationship between phase symmetries corresponding to a unique irreducible representation of the higher symmetry. Type II transitions are those in which continuous change of a structural parameter relates stable phases through a shared subgroup or supergroup intermediate. Any other transition (type III) can be effected through a chain of type I or II steps. There is experimental evidence that some ‘reconstructive’ transitions use transformation paths involving only a small number (3–4) of steps, without descent in symmetry to an amorphous intermediate. Such short pathways may be particularly important at high pressure. However, longer routes and less symmetrical transition states may be favoured kinetically. The shortest pathways between structures are readily derived by considering structural similarities and available lattice modes. The probable utilization of such routes provides a rationale for understanding observed stable and metastable behaviour, as shown by examples from *MX* and *MX*₂ systems and CaCO₃.

The predictions of this approach are readily tested using molecular dynamics simulations.

1. Introduction

Buerger (1951) classified structural phase transitions as *reconstructive* or *displacive*, depending on whether or not breakage of primary interatomic bonds was required in order to interconvert the crystal structures. There is a correlation with transformation mechanism in that reconstructive transitions are likely to involve heterogeneous nucleation, whereas new phases may nucleate homogeneously in a displacive transition. Thermodynamically, reconstructive transitions show discontinuities in first-order free-energy derivatives (entropy and volume) due to the significant change in atomic environments at the transition, whereas displacive transitions may be second-order in character. Even when a displacive transition is thermodynamically first order, the close relationship between the structures of the two phases makes it easy to visualize transformation occurring continuously, by variation of a few structural parameters. The first-order character then arises because these intermediate states are higher in energy at the transition than the structures of either stable phase.