## Nitrogen Contamination in Elastic Neutron Scattering

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**Abstract** Neutron diffraction measurements have been carried out on a single crystal of the iron-based superconductor system  $SrFe_{1.92}Ni_{0.08}As_2$ . Nitrogen gas sealed in the sample container was found to produce Bragg peaks over a limited range of temperature that were symmetrically positioned around the strongest magnetic Bragg peak in the system, giving the appearance of transition to an incommensurate magnetic state. These peaks were observed on warming but not on cooling, and were identified as structural in origin from the  $\beta$ -phase of solid N<sub>2</sub>. The details of this spurious scattering are presented.

### 1. Introduction

The most commonly observed effect of air scattering during a neutron scattering measurement is a contribution to the background, especially in inelastic measurements which require longer counting times. Another source of 'background', by which we really mean unwanted and/or unexpected cross sections observed in a measurement, is when exchange gas is used in sample environment equipment. Typically helium is employed as the exchange gas because it remains mobile for thermal conduction purposes at all temperatures (if sufficient helium is present) and has a small neutron cross section. Nevertheless, the scattering from liquid helium can be observed at low temperatures, below ≈4 K (Shirane et al., 2002, ch.6; Lynn, 1986). However. contamination by air, in particular diatomic nitrogen which scatters much more strongly than helium, can occur if the source of He itself is contaminated, the system used to introduce the exchange gas contains a significant amount of air, or the sample environment system leaks air into the

sample area. In this situation one might see changes in the background scattering at much higher temperatures, somewhere below 77 K depending on the partial pressure of N<sub>2</sub> (Shirane et al., 2002, ch.6). Moreover, as a classical diatomic van der Walls crystal, solid nitrogen exhibits solid-solid structural transitions (Mulder et al., 1998) that can also cause sharp changes in the background as well as peaks in the scattering that can be misidentified. Here we report some of the effects of having N<sub>2</sub> in the sample environment system during elastic neutron scattering measurements on a single crystal of the superconductor iron-based system SrFe<sub>192</sub>Ni<sub>0.08</sub>As<sub>2</sub> (SFN8A). The spurious changes observed include sudden changes in the Bragg intensities and the development of new 'incommensurate' Bragg peaks, in addition to the usual changes in 'background' scattering. The anomalous changes in the observed Bragg scattering are found to occur on warming but not on cooling, and furthermore depend on rate of change of the temperature. The overall behaviour can make it difficult to readily identify this scattering as spurious, as we will see below.



**Figure 1** Temperature dependence of the peak intensity of (a) the (0,0,2) nuclear Bragg peak, (b) the (1,0,3) magnetic Bragg peak and (c) the q=(1.184,0,3) 'incommensurate' Bragg peak, on warming (open red and green symbols) and on cooling (solid black symbols).

### 2. Experimental methods

The problem that was being investigated concerned the magnetic and structural transitions in phase the iron-based superconductor SrFe<sub>2-x</sub>Ni<sub>x</sub>As<sub>2</sub>. The system is tetragonal at room temperature, and undergoes an orthorhombic distortion at lower temperature, below which long range antiferromagnetic order develops (For a recent review, see Lynn & Dai, 2009). In measure the temperature order to dependence of the lattice parameters and the magnetic order parameter in SFN8A, neutron diffraction measurements were carried out on a 21 mg single crystal at the BT-7 and BT-9 triple axis spectrometers at the NIST Center for Neutron Research. A typical instrumental configuration was employed, using a neutron energy of 14.7 meV provided by pyrolytic graphite crystals as monochromator, analyzer (when employed) and For filter. the

measurements presented. Söller collimations of 60'-50'-S-50' (with no analyzer) were used on BT-7 and 40'-47'-S-40'-100' were used on BT-9. Polarized neutron measurements were carried out on BT-7 using He<sup>3</sup> polarizers (Chen et al., The sample was sealed in an 2007). aluminum sample can in a glove box with He as the intended exchange gas. The sample can was then mounted in a bottomloading closed cycle refrigerator (CCR). The lattice parameters are a = 5.5746 Å, b = 5.513 Å, and c = 12.286 Å at T=60 K.

#### 3. Results and discussion

An example of the intensity of the scattering on warming and cooling is shown in Fig. 1. The combined structural and magnetic transitions occur for this particular composition at ~140 K. For temperatures between this transition and  $\approx 80$  K we found a smooth change in the peak intensity of the (002) structural peak (Fig. 1(a)), and the development of the (103) magnetic peak (Fig. 1(b)). On cooling, typically the data are smooth and continuous all the way to low temperatures. However, on warming we observed sharp and dramatic changes in the intensities, indicating that a first-order transition has occurred. These data were taken without any motor movement, so that the peak intensity vs. temperature is displayed. However, we found similar abrupt changes Comparable data were in  $\theta$ -2 $\theta$  scans. obtained on other nuclear Bragg peaks such as (0,0,4), (2,0,2) and (4,0,0). As we will see below, a first-order transition has indeed taken place on warming, but not in the SFN8A crystal being investigated.

These changes were first observed on the magnetic (1,0,3) peak, and scans along the H direction then were carried out in the vicinity of the (1,0,3) peak, as shown in Fig. 2(a). The data revealed that, combined with the sudden reduction in the intensity of the (1,0,3) commensurate magnetic peak (Fig. 1(b)), two incommensurate peaks were observed symmetrically at  $(1\pm\delta,0,3)$ . Along the L direction, again two incommensurate peaks were observed at  $(1,0,3\pm\epsilon)$  (Fig. 2(b)), suggesting a change in



**Figure 2** Observed scattering on warming in the vicinity of the (1,0,3) magnetic Bragg peak. In addition to the commensurate (1,0,3) peak, 'incommensurate' peaks are observed at symmetric positions in (a) H scans at  $(1\pm\delta,0,3)$ and (b) L scans at  $(1,0,3\pm\epsilon)$ . (c) polarized neutron measurements on warming, analogous to the data shown in Fig. 1(c). The data reveal that these new peaks only occur in the non-spinflip channel, demonstrating that they are structural in origin rather than magnetic.

the magnetic structure. The symmetry in the position of the new peaks suggested that these are incommensurate magnetic peaks. Polarized neutron measurements, however, showed that these new peaks are only observed in the non-spin-flip channel as shown in Fig. 2(c), indicating that they are structural rather than magnetic in origin.

A general survey of the scattering in the vicinity of the magnetic (1,0,3) peak was then carried out, and revealed that this incommensurate scattering actually originates from two concentric powder rings. Fig. 3(a) shows one of the rings, which appears on warming but not on cooling (Fig. 3(b)). The positioning of these structural peaks symmetrically about the (1,0,3) peak in H and L scans is just an



**Figure 3** Contour plot of the ring of scattering from  $\beta$ -N<sub>2</sub> for |Q|=2.033 Å<sup>-1</sup> that appears on warming. The intensity and range of temperature where the ring is observed is dependent on the warming rate, and can be time-dependent depending on the final equilibrium temperature. (b) On cooling the ring is not observed.

unfortunate coincidence for this particular system. If only one peak had been observed about the (1,0,3) then the scattering would have been quickly categorized as spurious in nature, but the observed symmetry suggested initially that the scattering was genuine.

The intensity of the scattering on the ring position (1.184,0,3) is shown in Fig. 1(c) (and Fig. 2(c)) as a function of temperature. We see that the scattering starts to develop around 30 K when the temperature is changed by 0.2 K for a counting time of 20 s, while it starts to develop around 40 K when warming at the faster rate of 0.5 K every 20 s. The powder rings of scattering abruptly disappear at  $\approx 60$  K, where the single crystal Bragg peak intensities suddenly change as shown in Fig. 1. The appearance of the powder rings happens at different temperatures depending on the warming rate; all the data with red (open) symbols in Fig. 1 were taken at the same warming rate in the same CCR. The data clearly show that the sudden change in the single crystal Bragg intensity happens when the powder rings disappear. To establish with certainly that all these effects are due to  $N_2$  in the sample can, we carried out measurements with pure He sealed in the can, and then with pure  $N_2$ . All the



**Figure 4** (a) Rocking scan (A3) of the (0,0,4) structural Bragg peak for the crystal, which was inadvertently sealed with some air inside. There is a sudden shift in position in the temperature range between 60 K and 80 K. (b)This anomalous shift in orientation of the crystal does not occur if the sample can is sealed with pure He. (c, d) Peak intensity for the ring and (0,0,2) Bragg peak on warming, with the sample can sealed in air (squares), or with pure helium gas (circles). The anomalous scattering is only observed when air is in the sample can.

anomalous phenomena were observed with  $N_2$  in the sample can, and disappeared when the He-sealed sample was measured, as shown in Fig. 4.

Solid nitrogen is known to have at least five phases up to 20 GPa:  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\varepsilon$ phases (Mulder *et al.*, 1998). The  $\gamma$ -,  $\delta$ - and  $\varepsilon$ -phases appear when pressure is applied and therefore are not of interest here since the sample can is sealed at room temperature at atmospheric pressure and then cooled. The crystal structure is cubic (Pa3) for  $\alpha$ -N<sub>2</sub> and hexagonal (P6<sub>3</sub>/mmc) for  $\beta$ -N<sub>2</sub>, and at equilibrium vapor pressure the  $\alpha \leftrightarrow \beta$  phase transition occurs at  $T_{\alpha \leftrightarrow \beta}$ =36 K (Scott, 1976). For the temperature range of interest here the two rings we observe at  $|\mathbf{Q}|=2.033$  Å<sup>-1</sup> and 1.808 Å<sup>-1</sup> can be identified as the (1,0,1) and (1,0,0) peaks for hexagonal  $\beta$ -N<sub>2</sub>, which correspond to d=2.964 Å and d=3.334 Å, respectively (Schuch & Mills, 1970). For hexagonal β- $N_2$ , the (1,0,1) peak has the strongest intensity, which is about 3.8 times larger than the (1,0,0), in agreement with observation. A more complete listing of dspacings and calculated intensities is given in Table 1. We note that the transition temperature  $T_{\alpha\leftrightarrow\beta}$  strongly depends on the residual order above the transition (Scott, 1976), and it is also reported that the  $\alpha\leftrightarrow\beta$  transition has hysteresis and takes as long as 10 hours for the system to equilibrate and reliably measure the intrinsic  $T_{\alpha\leftrightarrow\beta}$  (Heberlein *et al.*, 1970). Hence for the present data the warming and cooling rates were too fast to produce an equilibrium phase.

Finally we address the issue of the difference between the warming and cooling cycle. We were able to find a few cooling rates where we observed some small changes in the intensities on cooling, but the dramatic changes were only observed on warming. We expect the reason for this is because when cooling, the container itself is at a lower temperature than the sample, which cools via the exchange gas in the container. Thus at the appropriate temperature the nitrogen inside the sample can will condense onto the walls of the container, where it won't be observed in the scattering experiment when the incident and scattered beams are suitably restricted. On warming, on the other hand, the walls will be at a higher temperature than the sample. The nitrogen will then evaporate from the walls and condense onto the sample, where the polycrystalline  $N_2$ can scatter neutrons into the detector. We remark that there is a large thermal expansion of N<sub>2</sub> both at the  $\alpha \leftrightarrow \beta$  transition as well as below ≈60 K just before it liquefies (Krupskii et al., 1975), which appears to affect the alignment of the sample. These alignment changes are  $\approx 0.1$ - $0.2^{\circ}$ , which is enough of a misalignment of the crystal to perturb the Bragg peak intensities. We note that the properties of these 1:2:2 systems are quite sensitive to any stresses imposed on the crystal (Lynn & Dai, 2009), so for these iron-based materials the crystals could not be rigidly thus allowing the mounted.  $N_2$ condensation and structural transitions to perhaps more easily affect the alignment of the crystal.

### 4. Conclusion

In summary, we have observed anomalous scattering for this iron-based 1:2:2 system due to N<sub>2</sub> condensing on the sample. The phase transitions of the N<sub>2</sub> with temperature can affect the alignment of the crystal, and also produce powder Bragg peaks of comparable intensity to the magnetic peaks. The structural powder peaks turned out to be symmetrically located about the strongest magnetic reflection, initially suggesting that these peaks were authentic magnetic peaks. These problems can occur in a sealed sample container if for some reason the helium exchange gas is not sufficiently pure, or for top-loading sample environment systems that develop a leak. It is hoped that the present results will alert investigators to quickly identify these problems when they occur in the future.

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### References

Chen, W. C., Armstrong, G., Chen, Y., Collett, B., Erwin, R., Gentile, T. R., Jones, G. L., Lynn, J. W., McKenney, S., and Steinberg, J. E. (2007). Physica B 397, 168. Heberlein, D. C., Adams, E. D. and Scott, T. A. (1970). J. Low Tem. Phys., 2, 449. Krupskii, N., Prokhvatilov, A. I., and Erenburg, A. I. (1975). Fizika Nizkikh Temp., 1, 359. Lynn, J. W. (1986). Physica 136B, 117. Lynn, J. W. and Dai, P. (2009). Physica C 469, 469. Mulder, A., Michels, J. P. J., and Schouten, J. A. (1998). Phys. Rev. B, 57, 7571. Schuch, A. F. and Mills, R. L. (1970). J. Chem. Phys. 52, 6000. Scott, T. A. (1976). Physics Report, 27, 89. Shirane, G., Shapiro, S. M., and Tranquada, J., Neutron Scattering with a Triple-Axis National Spectrometer (Brookhaven Laboratory, 2002), Chap. 6, p 162.

Table 1	Observed and calculated d-spacings and Bragg peak integrated intensities for hexagonal β-
N <sub>2</sub> (space	group $P6_3/mmc$ ) based on the structure from reference [7]. The calculated intensity for the
(1,0,1) pea	ak is defined to be equal to the observed value to facilitate comparison.

hkl	100	002	101	102	110	103	112
$d_{calc}(\text{\AA})$	3.344	3.132	2.950	2.286	1.931	1.771	1.643
$d_{obs}(\text{\AA})$	$3.341 \pm 0.005$		2.959±0.006				
$I_{calc}$	148	166	≡581	49	30	28	19
$I_{obs}$	152±25		581				