IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Anomalous shift of magnetic diffuse scattering studied by neutron diffraction

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys.: Condens. Matter 21 285402

(http://iopscience.iop.org/0953-8984/21/28/285402)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 29/05/2010 at 20:36

Please note that terms and conditions apply.

J. Phys.: Condens. Matter **21** (2009) 285402 (6pp) doi:10.1088/0953-8984/21/28/285402

Anomalous shift of magnetic diffuse scattering studied by neutron diffraction

K Prokeš[1], G H Lander[2] and N Bernhoeft[3]

[1] Helmholtz Centre Berlin for Materials and Energy, SF-2, Glienicker Straße 100, 14109 Berlin, Germany
[2] European Commission, JRC, Institute for Transuranium Elements, Postfach 2340, 76125 Karlsruhe, Germany
[3] CEA Grenoble, DRFMC/SPSMS, F-38054 Grenoble, France

E-mail: prokes@helmholtz-berlin.de

Received 24 February 2009, in final form 5 June 2009
Published 18 June 2009
Online at stacks.iop.org/JPhysCM/21/285402

Abstract
Neutron diffraction results, in the vicinity of the magnetic phase transition of USb and MnF_2, are reported. The thermal evolution of the magnetic diffuse signal and nuclear Bragg reflections demonstrate that the centre of gravity of the magnetic signals does not lie at the predicted position as calculated from nuclear reflections. This phenomenon, called the q-shift, was first found using resonance x-ray scattering (RXS). The present results show that, (i) the effect is not an artefact of RXS and is also found with neutrons (ii) that the effect arises from the bulk of the sample and is not restricted to the near surface layer (∼2000 Å) associated with the RXS probe in actinide systems, (iii) the effect is not restricted to actinide compounds.

1. Introduction

Recently it has been shown by resonant x-ray scattering (RXS) that magnetic scattering in the presence of short-range order is displaced in scattering angle both with respect to its position in a state of long-range order and its fiducial Bragg charge peaks. The effect, known as the q-shift, has been seen in numerous antiferromagnetically ordered actinide materials, namely UO_2, USb, UPd_2Al_3 and URu_2Si_2 [1] and discussed in the light of a generalized Berry phase correction [2]. X-ray synchrotron diffraction offers high q-space resolution and the effects are clearly larger than the resolution uncertainty. However, this scattering method also has severe drawbacks. Due to its small penetration depth, it only probes the near surface and due to alignment difficulties one cannot easily compare results obtained in different Brillouin zones.

The following experimental questions still remain open. First, whether the observations are representative of bulk or near surface of the material, this may be addressed by neutron diffraction, which probes the whole sample volume. Second, how results obtained in different zones compare with each other. Finally, a more general question arises: is such an effect a general feature of antiferromagnetic materials, or does it exist in other non-actinide systems. Of course, the resolution required for these experiments is at the limit available with diffractometers using thermal neutron wavelengths. This makes the experiments very hard and probably accounts for the fact that this q-shift has not, up to now, been reported in neutron diffraction.

In this paper we describe the neutron diffraction results obtained with high-quality single crystals of USb and MnF_2.

2. Experimental details

We have chosen USb and MnF_2 as two model systems for the following reasons. First, both systems have been well characterized and studied by neutron and x-ray scattering techniques. Second, the effect of an anomalous q-shift discussed in this paper has already been observed in USb by x-ray resonant scattering [1], so it exists in this system and third, large MnF_2 crystals of excellent quality are available. The USb crystal used in our studies had the shape of a cube with a ∼3 mm edge length. The crystal of MnF_2 (provided by W Jauch) was much larger, being a parallelepiped with dimensions approximately $5 \times 10 \times 18$ mm^3.

USb has the NaCl cubic type of structure with $a = 6.21$ Å. For this structure lattice reflections of the type $(hh0)$ with h odd are absent. USb is an antiferromagnet with the Néel temperature $T_N = 214$ K and a commensurate type-I triple-**k** magnetic ordering [3]. The U magnetic moments of 2.85 μ_B

 © 2009 IOP Publishing Ltd Printed in the UK

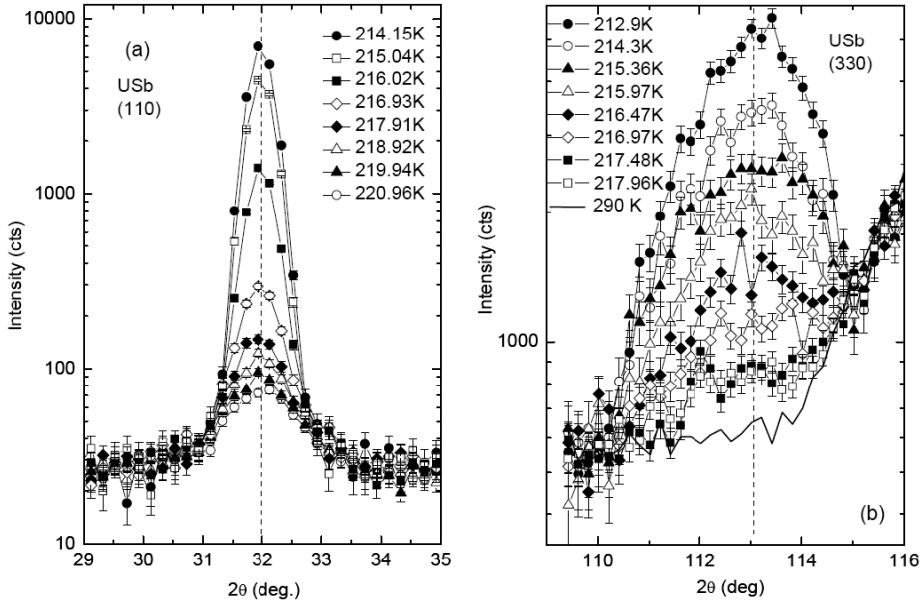

Figure 1. Experimental diffraction profiles measured at the position of the USb (a) (110) and (b) (330) reflections by the single detector at various temperatures in a semi-logarithmic scale. The dashed lines represent the fitted position of the Bragg component at the lowest measured temperature.

give rise to reflections of the $(hh0)$ type with h odd [4]. The sample was oriented with a cube axis along the rotation axis of the diffractometer. In this configuration it is possible to detect reflections of a pure nuclear (e.g. (220) reflection) and a pure magnetic (e.g. (110) and (330)) origin.

MnF_2 crystallizes in a simple tetragonal rutile-type crystal structure with space group $P4/mnm$. The tetragonal unit cell has dimensions $a = 4.874$ Å and $c = 3.310$ Å at room temperature. Below $T_N \sim 67.7$ K, MnF_2 orders antiferromagnetically with a magnetic unit cell of the same size as the crystallographic one and is an example of a simple two-sublattice antiferromagnet, where the magnetic moment in the centre of the unit cell is antiparallel to the moment at the corners. The moments are aligned parallel to the c axis. Magnetic peaks occur at (100) and (300), whilst the (200) reflection is of nuclear origin only [5].

The neutron diffraction experiments were performed on the double-axis E4 diffractometer installed at the Helmholtz Centre Berlin (formerly Hahn-Meitner-Institute). This instrument is equipped with a graphite (002) monochromator at a take-off angle of 42.5° and two graphite filters, offering the incident neutron wavelength of $\lambda = 2.44$ Å with residual $\lambda/2$ contamination of the order of 10^{-4}. The single-crystal samples were glued to an aluminium holder and placed, in the desired orientation, into a standard ILL-type orange cryostat. The data were collected with progressively increasing counting times ranging from 10 min for data taken below the magnetic phase transition up to 24 h for data collection far above the T_N. Mostly θ–2θ scans were collected. There were two experiments on USb, both of which were performed with a single detector and two on MnF_2, one of which was performed with an area detector covering a scattering angle 2θ of about 18°, 9° above and 9° below the scattering plane. The total solid angle covered in the experiment was 0.11 Sr.

3. Experimental results

3.1. USb

In figure 1 we show representative raw rocking curves of the (110) and (330) magnetic reflections measured at various temperatures and normalized to monitor. For clarity, the data are represented on a semi-logarithmic scale. Unfortunately, the data for the (330) reflection are contaminated by the proximity of an aluminium powder line arising unavoidably from the cryogenic environment. For the analysis, the (330) data have been corrected for this defect by subtracting the data measured at 290 K, i.e. far above the T_N. The (110) and corrected (330) profiles were fitted either to a Gaussian profile for data far below the T_N, a Lorentzian for data far above the T_N or to a sum of both components in the vicinity of the magnetic phase transition. For the analysis of the (220) reflection a Gaussian profile was used. The background was allowed to have a slope. It should be stressed that no distortion from cubic symmetry occurs at the magnetic phase transition T_N. This is a consequence of the triple-**k** type of magnetic ordering, and was verified by the synchrotron experiments reported in [1].

Figure 2 gives the temperature dependences of the fitted parameters for the (110) reflection: panel (a) records the intensity, (b) the peak centre of mass position (c) the width. As can be seen in panel (b), on heating, the position of the signal remains constant (to a temperature that is approximately 2 K above the value of the magnetic phase transition given in the literature) and then starts to decrease. At the same time, the width of the signal (panel (c)) starts to increase significantly. At 222 K, i.e. about 8 K above the T_N, it is more than three times larger than at the lowest measured temperature, at which point it is resolution limited. The critical scattering in USb was examined many years ago, but the present paper does not enter into these discussions [6].

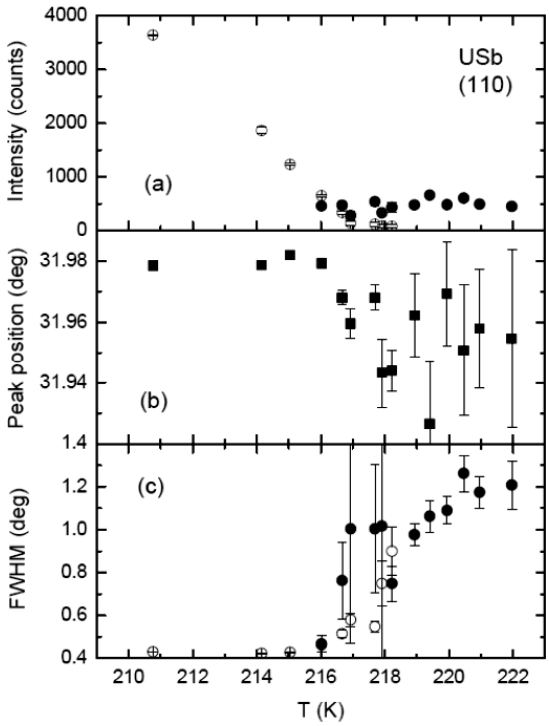

Figure 2. The temperature dependences of the integrated intensity (a), position (b) and the full width at the half maximum—FWHM (c) obtained by fitting the Gaussian (open points) and/or Lorentzian (filled circles) profiles to the signal detected at the magnetic (110) peak of USb. The position was constrained to be equal for the Gaussian and Lorentzian signals (filled squares in (b)).

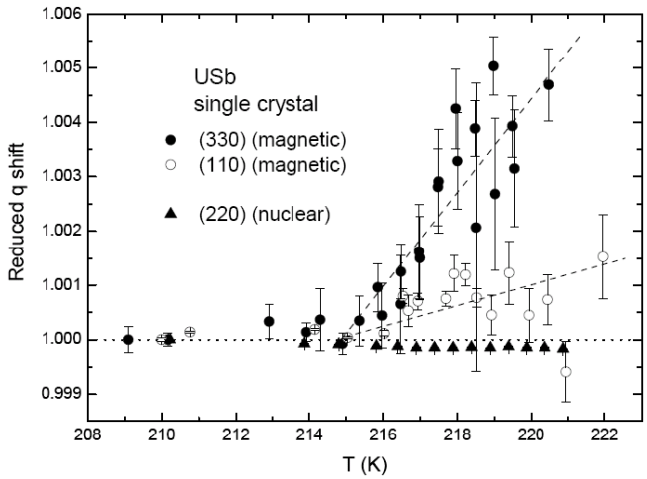

Figure 3. The temperature dependence of the reduced shift in the position of the signal recorded around the reflection condition for the (110), (220) and the (330) reflections of USb. Note that the small change in the position of the (220) reflection has the opposite sign to those of the (110) and (330) reflections, and that the (330) shift is significantly larger than that of the (110) reflection.

The fitted parameters of a Gaussian profile on the nuclear (220) reflection yield a nearly temperature independent intensity and width with a very small change in the position due to thermal expansion. The analysis of the (330) reflection is difficult mainly because of the weaker signal due to the reduced magnetic form factor of this reflection when compared to that of the (110) [4], and to the worse resolution. To obtain sufficient intensity above the T_N, data collection times for as long as 24 h per temperature were used. The shift of the peak centre of mass position for the (330) is systematically larger than in the case of the (110) magnetic reflection. In order to compare all three sets of data we have calculated the relevant d-spacing and normalized it to the d-spacing value at the lowest measured temperature. The resulting temperature dependence of the so-called normalized q-shift is depicted in figure 3. The obvious experimental finding is that (a) the nuclear (220) reflection shows a small shift (due to the thermal expansion) that is in the opposite sense to that of the magnetic reflections (110) and (330), and (b) that the (330) shift is larger than the shift found for the (110) reflection. The fit to the data shown in figure 3 reveals that the ratio between the (330) and (110) reflection shifts is roughly equal to four. Comparing this with figure 2 of [1], we see that the shift over the region ∼5 K above T_N is 4×10^{-4} in the x-ray case for the (003) reflection. This is close to the order of magnitude of the (110) reflection in the neutron case, and smaller than shown for the (330) reflection.

The quality of the data is not good enough to draw quantitative conclusions, except that there does seem to be a clear correlation between the magnitude of the q-shift and the width of the signal: the wider the signal, the larger q-shift. Whether the relationship is linear, quadratic or of another form, cannot be deduced from these results. The x-ray experiments of [1] are clearly more quantifiable.

3.2. MnF_2

In figure 4 we show selected profiles at various temperatures measured at the position of the (100) and (300) magnetic reflections with the 2D detector, projected on to the scattering plane and normalized to the monitor count. For clarity, the data are shifted for each subsequent temperature and shown on a semi-logarithmic scale. As can be seen also for MnF_2, the peaks change in position and shape with increasing temperature from a Gaussian dominated to a Lorentzian profile across the magnetic phase transition. This is in contrast to the (200) reflection that changes neither in shape nor position. A Lorentzian contribution in the case of the magnetic reflections is present even below T_N, as is well known from the pioneering work on the critical scattering of MnF_2 [6]. By moving the diffractometer off the peak position, we have determined $T_N = 67.4(1)$ K, in good agreement with values in the literature [7–10].

Analysis of the peaks represented by the sum of a Gaussian and Lorentzian profile is complicated by the strong coupling of the parameters. We have tried several models. Apart from model-(i) with all parameters as free variables, we have used model-(ii) with the Gaussian and Lorentzian profiles constrained to have the same central position and model-(iii) with the position for the Lorentzian contribution fixed to a value obtained from fits outside the Bragg peak reflection condition. Model-(iv) with a Gaussian profile below and a Lorentzian above the magnetic phase transition has been examined as well. Whilst the best fits were obtained for the unconstrained model-(i) (which also gives the

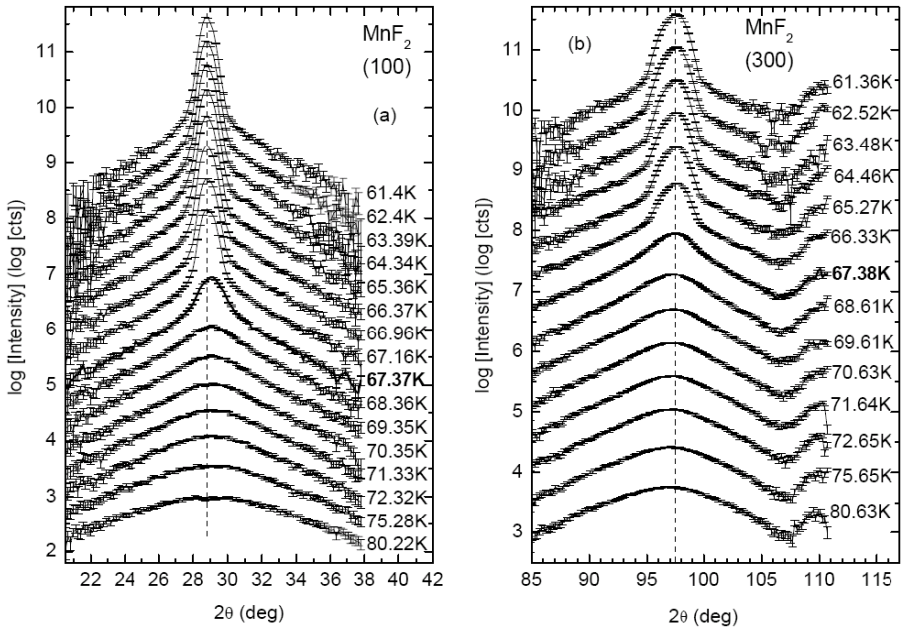

Figure 4. Representative experimental profiles recorded at the position of the MnF_2 (a) (100) and (b) (300) magnetic reflections by the 2D detector at various temperatures. For clarity, the data are shifted for each subsequent temperature and shown in logarithmic scale. For the (300) reflection, the signal is contaminated on the right side by scattering from the sample environment. The T_N is denoted by bold labels aside and thicker lines.

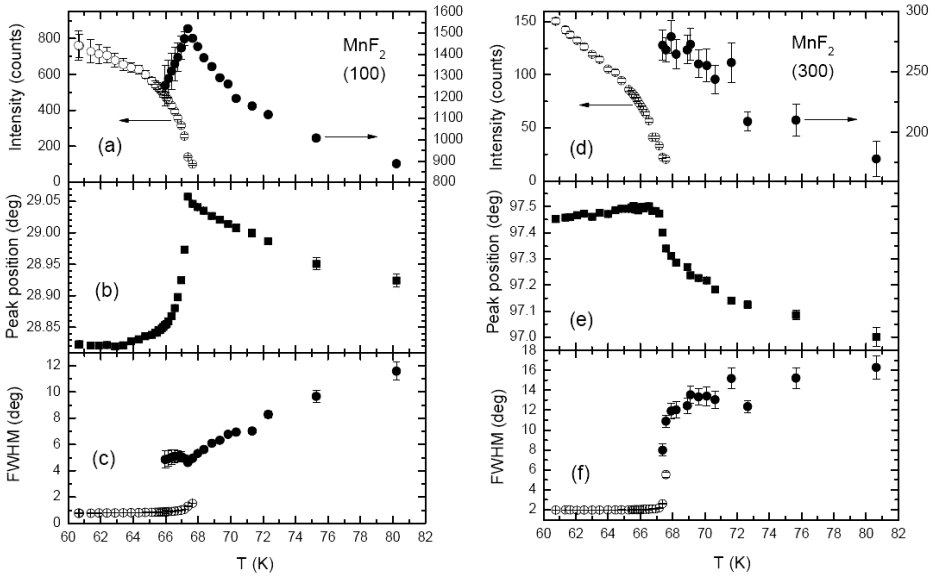

Figure 5. The temperature dependences of the integrated intensity obtained by fitting the Gaussian (open points) and/or Lorentzian (filled circles) profiles to the measured intensities from the MnF_2 crystal, as measured by the 2D detector, is shown for the (100) reflection in panel (a). The two functions are constrained to have the same peak centre. Its temperature dependence is shown for the (100) reflection by filled squares in (b). The temperature dependences of the full width at the half maximum—FWHM of the two components is shown for the (100) reflection in panel (c). Analogous temperature dependences for the (300) reflection are shown on the right in panels (d)–(f).

largest parameter uncertainty), the main qualitative features are independent of the actual fitting routine used to describe the data. The results obtained from model-(ii) are representative. The background was a free parameter in all the models.

In figure 5 we show the temperature dependences of the intensity, position and the full width at the half maximum (FWHM) obtained by fitting Gaussian and Lorentzian profiles constrained to have the same peak centre to the signal recorded at (and around) the MnF_2 (100) reflection, as shown in figure 4(a). Analogous temperature dependences of the fitted (300) peak parameters are shown in (d)–(f) on the right-hand panel of figure 5. The intensity of both reflections (as represented by the Gaussian component and shown by open symbols) decreases with increasing temperature and vanishes above T_N. It can be described by a phenomenological dependence of the form $I = I_0(1 - T/T_N)^{2\beta}$. This function,

which was developed to describe the data in a critical region close to the phase transition, gives a good description of the data. The fit to data above 66 K yields $T_{N(100)} = 67.423 \pm 0.003$ K and $T_{N(300)} = 67.58 \pm 0.02$ K, values that are 0.1–0.2 K lower than the T_N value found by Brückel *et al* [7] in their non-resonant synchrotron x-ray scattering experiment, but in very good agreement with result of Schulhof *et al* [8, 9]. We do not list, however, any fitted value for β as it is well known that its reliable determination is impossible without extinction corrections that are important in neutron experiments on MnF_2.

The intensity of the Lorentzian components (closed symbols) peaks at T_N and decreases below and above the magnetic phase transition. The Bragg-component FWHM stays almost constant up to the temperature of the magnetic phase transition and then increases abruptly. In the same temperature region the Lorentzian parts that start to dominate the signal have their smallest FWHM. With increasing temperature the FWHM increases significantly up to ∼15 K above T_N, indicating the decrease in the magnetic correlation length. Its value is at 80 K about ten times larger than the resolution limited values of the Bragg parts described by the Gaussian profiles.

The most striking result is the temperature dependence of the (100) and (300) peak positions that are clearly different. Whereas the (100) reflection exhibits a non-linear shift below the T_N, the (300) reflection shows a more linear dependence that is, in the studied temperature range, much smaller. The much better resolution available at the (100) position may allow effects of magnetostriction to be observed and to be responsible for such an observation below T_N. Above T_N both peak positions decrease in 2θ as a function of increasing temperature. The decrease is much larger at the (300) reflection.

The temperature dependence of the reduced d spacing, calculated from the Bragg law and normalized to the value obtained at the T_N, is shown in figure 6(a). Although having slightly different values for T_N in the two experiments we can conclude that the reduced q-shift has, for all the four data sets, (i.e. two experiments with two magnetic reflections each) a similar initial slope (between the T_N and 70 K) that is about $(7 \pm 1)10^{-5}$ K^{-1}. Plots of the q-shift of the reflections versus the full width at the half maximum (FWHM) are given in figure 6(b).

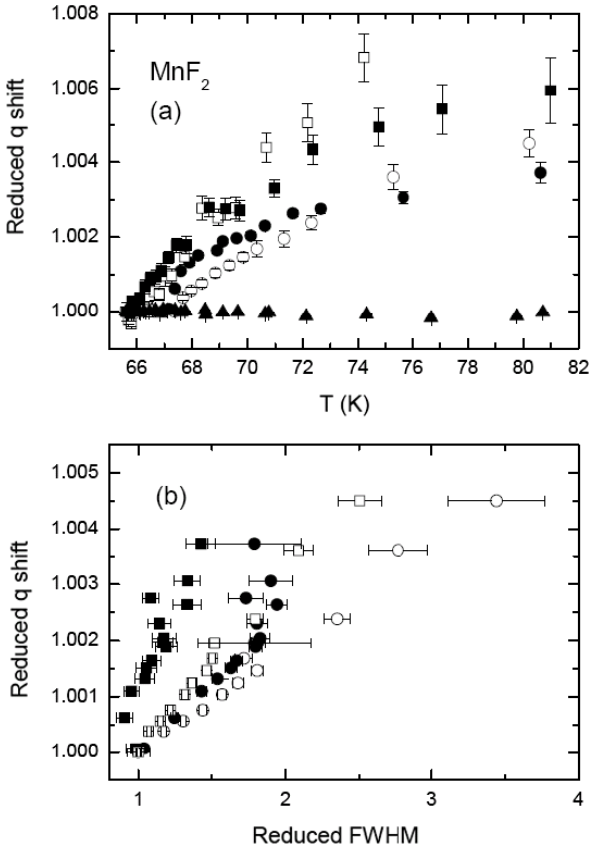

Figure 6. (a) A portion (data above the T_N) of the temperature dependences of the reduced q-shift, normalized to that at T_N for the magnetic reflections in MnF_2, as measured in two different experiments (circles and squares). (b) The reduced q-shift plotted against the FWHM divided by the FWHM at the T_N (reduced FWHM) with temperature as an implicit parameter. Open circles and squares correspond to the (100) reflection, closed to the (300) reflection; solid triangles to the (200) nuclear reflection.

4. Discussion and conclusions

Before turning to a discussion of the results of the present study, we would like to mention two additional diffraction effects that have sometimes been confused with the q-shift as presented in [1] and this paper.

The first effect is known as the phenomenon of the 'two-length scales'. This was investigated extensively in the 1990s, and the observation is that the critical scattering (i.e. the intensity just above T_N) consists of more than one component. Usually, the data were fitted to *two* components, and the thrust of the studies was that the behaviour of the magnetic correlations at the surface (or skin) was different from that of the bulk. Good examples are work on Tb [11] and more recent work on a relaxor ferroelectric [12]; the latter paper contains extensive references to this subject. However in these studies, the position in $\boldsymbol{Q}$ of the critical scattering was never an issue. In many cases transverse scans were performed (e.g. in [11]) and these would not observe the q-shift as it appears only in the *longitudinal* scans. We do not in our study address the exact form of the critical scattering in either USb or MnF_2, as they have both been studied previously; our interest is simply in the *position* of the peaks. Thus, our observations are fundamentally different from those in the 'two-length scale' studies.

The second effect that has been confused with the present observations is in the case where materials show incommensurate magnetic fluctuations, and then order with a commensurate wavevector. In this case, for USb for example, there would be six centres of scattering around the (110) position in reciprocal space, all displaced by an amount δ from (110) along the cube axes, where the incommensurate fluctuations have a wavevector $(1 - \delta)$. Depending on the neutron resolution and the magnitude of δ, these might or might not be observed; however, they are not observed with the superior resolution of the RXS experiments [1]. The

important point to note is that incommensurate fluctuations must be symmetrically located about the position of the (commensurate) magnetic zone centre. In the case of the q-shift this is clearly *not* the case [1]. Interestingly, such incommensurate fluctuations do exist in UAs, a material very similar to USb, and one that orders at low temperature in the same magnetic structure as found in USb. Studies were reported in the 1980s for UAs [13], and such phenomena exist also in other materials. This is not what is observed in the study of the q-shift.

There were a number of aims for the present experiments. The first was to see whether the unusual results using resonant scattering of x-rays reporting the q-shift of the antiferromagnetic peaks near the respective ordering temperatures in [1] were observable with neutron scattering. Our results show that such effects exist also in neutron-scattering experiments, excluding those where the results are related to the nature of the RXS sample-probe interaction, and especially effects at the near surface (penetration depth ∼2000 Å) of the samples.

The second aim was to determine whether the effects were somehow related to the actinide nature of the samples reported in [1]. In the RXS technique the enormous enhancement of the magnetic scattering signal at the actinide M edges allows a number of important experiments to be performed, and recently the q-shift has also been observed in a neptunium antiferromagnet [14]. The present neutron experiments show clearly that this phenomenon is not confined to actinides, but is related to the incipient formation of the antiferromagnetic state with long-range order. As a further confirmation we should mention that experiments with soft x-rays tuned to the transition-element L edges (wavelengths of up to 17 Å) have also seen such q-shifts [15]. However, the difficulty in such experiments is that frequently a charge peak *cannot* be seen as a fiducial marker, so these observations cannot be fully exploited.

The third aim was to measure more than one reflection at different momentum transfers and obtain an idea of the momentum dependence. In this respect, we have not been able to bring any quantifiable information because of the limitations of resolution. Neutron diffractometers have their best resolution at the focusing condition (when the Bragg angle of the monochromator is the same as that of the sample reflection) so that we find the overall resolution is not good enough to make quantitative comparisons. Qualitatively, it is clear that the effect *increases* with increasing momentum transfer, and we hope that these experiments motivate other efforts to obtain more precise experimental results.

A more complete attempt should also be made to examine the theory of the scattering process to understand the q-shift, and whether the suggestions made in [1] are correct.

Acknowledgment

We thank W Jauch from HMI Berlin, for providing the MnF_2 crystal used in the present experiment.

References

[1] Bernhoeft N *et al* 2004 *J. Phys.: Condens. Matter* **16** 3869
[2] Berry M V 1984 *Proc. R. Soc.* A **392** 45
[3] Lander G H and Burlet P 1995 *Physica* B **215** 7
[4] Lander G H, Mueller M H, Sparlin D M and Vogt O 1976 *Phys. Rev.* B **14** 5035
[5] Erickson R A 1953 *Phys. Rev.* **90** 779
[6] Lander G H, Sinha S K, Sparlin D M and Vogt O 1978 *Phys. Rev. Lett.* **40** 523
[7] Brückel Th, Lippert M, Köhler T, Schneider J R, Prandl W, Rilling V and Schilling M 1996 *Acta Crystallogr.* A **52** 427
[8] Schulhof M P, Heller P, Nathans R and Linz A 1970 *Phys. Rev.* B **1** 2304
[9] Schulhof M P, Heller P, Nathans R and Linz A 1970 *Phys Lett.* **24** 1184
[10] Hohlwein D 2002 *Appl. Phys.* A **74** (Suppl.) S740
[11] Gehring P, Hirota K, Majkrzak C F and Shirane G 1993 *Phys. Rev. Lett.* **71** 1087
[12] Stock C, Xu G, Gehring P M, Luo H, Zhao X, Cao H, Li J F, Viehland D and Shirane G 2007 *Phys. Rev.* B **76** 064122
[13] Sinha S K, Lander G H, Shapiro S M and Vogt O 1980 *Phys. Rev. Lett.* **45** 1028
Sinha S K, Lander G H, Shapiro S M and Vogt O 1981 *Phys. Rev.* B **23** 4556
[14] Detlefs B, Wilkins S B, Caciuffo R, Paixão J A, Kaneko K, Honda F, Metoki N, Bernhoeft N, Rebizant J and Lander G H 2008 *Phys. Rev.* B **77** 024425
[15] Wilkins S 2006 private communication