$U(As_{1-x}Se_x)$ solid solutions. II. New magnetic phase for $0.18<x<0.22$

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We further characterize the extra diffraction peaks reported for $0.18<x<0.22$ in the $U(As_{1-x}Se_x)$ solid solutions in the previous paper. A model based on the spin slip hypothesis is developed that suggests that a small volume ($\sim 1\%$) of the crystal can be characterized in the spin-addition state, i.e., the regular $k=1/2$ $(++--)$ repeat is interrupted by compensating + and − ''faults'' that are inserted into the magnetic structure. The spacing between these faults is between 20 and 40 unit cells, depending on the temperature and composition, x. We suggest that these spin-addition volumes form the interfacial region between the high-temperature 3**k** and the low-temperature, 2**k** magnetic structures, both with $k=1/2$.

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I. INTRODUCTION

In the previous paper,[1] hereafter denoted as I, we have reported a series of resonant x-ray magnetic scattering (RXMS) and neutron-diffraction experiments that have identified a new phase in the $UAs_{1-x}Se_x$ solid solutions. This new phase exists over a narrow composition range $0.18<x<0.22$ (see Fig. 12 of I) and coincides almost exactly with the phase boundary between the double-**k** (2**k**) magnetic structure found at lower x and the triple-**k** (3**k**) structure found at high x (see Fig. 1 of I for these structures). The new phase is characterized by the presence of the type-IA $(++--$ arrangement of ferromagnetic components) $k=1/2$ magnetic structure, but also by the presence of a much weaker ($\sim 1\%$), and temperature dependent, diffraction peak at $k_m \sim 0.44$ (reciprocal lattice units; rlu). This weaker peak is magnetic, as determined by its dependence on photon energy at the uranium M_4 edge, and first appears around 60 K, usually with a maximum at $\sim$45 K, and then decreases in intensity as the temperature is lowered. It has also been observed with neutron diffraction to have the same intensity ratio with the $k=1/2$ reflection and is thus a bulk effect. The intensity of this extra peak is too small to have been observed in previous studies with polycrystalline samples,[2,3] and, in the previous work on single crystals,[4] was missed because of its unusual dependence on x and temperature. In this paper, we describe in more detail the extra features in the diffraction pattern and suggest a possible explanation for its existence.

II. CHARACTERIZATION OF MODULATION

We present in Fig. 1 the result of a RXMS reciprocal lattice scan along **c*** for the $x=0.20$ sample at 12 K. The two peaks are modeled as Lorentzians. In Figs. 2 and 3 we show the temperature dependence of (a) the wave vector, (b) the full width at half maximum, and (c) the intensity of the two diffraction peaks in the $x=0.18$ and $x=0.20$ samples, respectively. We note a strong similarity in the data from both samples (as noted in I, two samples of $x=0.20$ made at different times gave identical results). In particular, the wave vector of the additional diffraction peaks tends to decrease with decreasing temperature, the width tends to decrease, and in both samples the maximum of its intensity approaches 1% of the main ($k=1/2$) modulation. At 45 K, $k_m \sim 0.45$ and the width is of the order 0.01 rlu for both samples. A distinct difference between the data for the two samples is that the modulation ceases to exist below 40 K for the $x=0.18$ sample. Interestingly, the width broadens as the intensity decreases. In contrast, the data for the $x=0.20$ sample show the modulation to remain at low temperatures. In fact, the intensity and width remain constant and the wave vector remains close to $k_m=0.44$.

III. SPIN SLIPS AND SPIN ADDITIONS

We model these extra diffraction peaks by consideration of the complex diffraction pattern observed for single-crystal holmium.[5] In the first x-ray experiments on Ho an unusual series of periodicities in the magnetic modulation was ob-

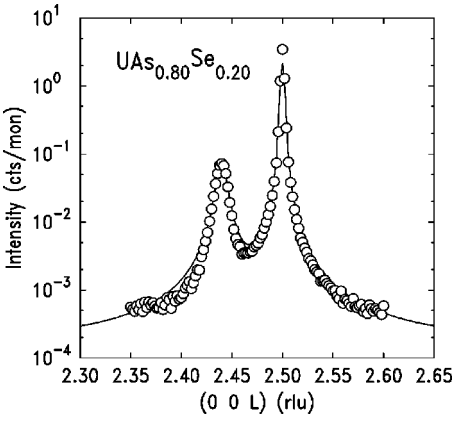

FIG. 1. A reciprocal space scan along **c*** for the $x=0.20$ sample at 12 K. These data about the $(0\ 0\ 2+k)$ position show the main commensurate ($k=0.5$), and the extra incommensurate ($k_m \sim 0.44$) magnetic peaks. The solid line is a fit to the data with two Lorentzian functions.

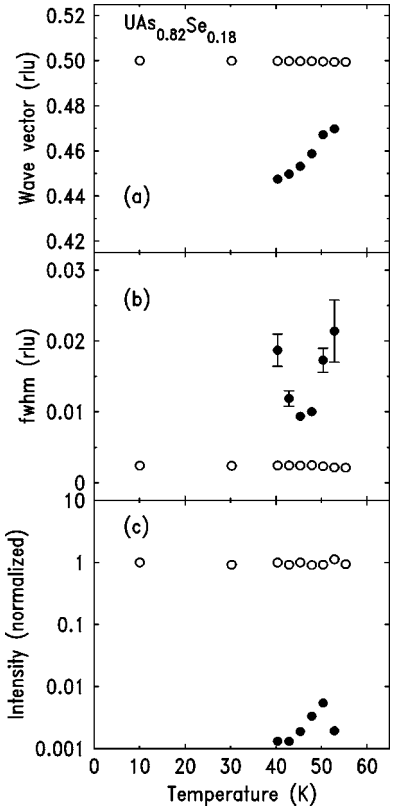

FIG. 2. The temperature dependence of (a) the wave vector, k, (b) FWHM, and (c) the intensity of the two diffraction peaks of the $x=0.18$ sample from reciprocal lattice scans along **c*** around (0 0 2+k). The intensity of the $k=1/2$ component has been normalized to 1 in panel (c).

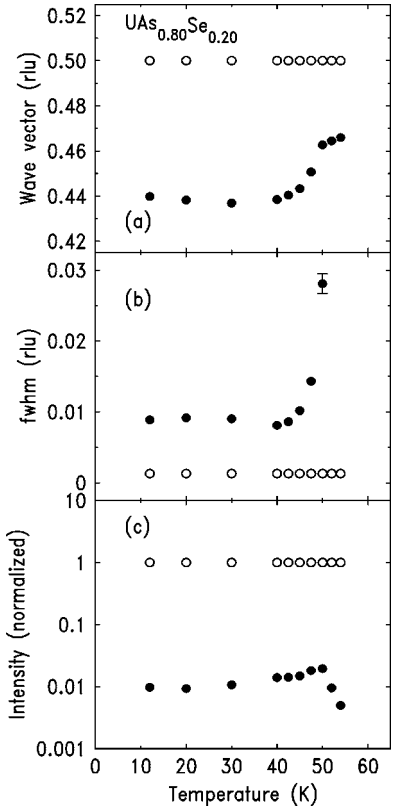

FIG. 3. The temperature dependence of (a) the wave vector, k, (b) FWHM, and (c) the intensity of the two diffraction peaks of the $x=0.20$ sample from reciprocal lattice scans along **c*** around (0 0 2+k). The intensity of the $k=1/2$ component has been normalized to 1 in panel (c).

served, which was explained by Gibbs *et al.*[5] to be a consequence of ''spin slips'' in the spiral arrangement of moments in the magnetic structure. The spin slip arises when the regular progression of the spiral structure is interrupted by two consecutive spins along the spiral arrangement, which have a phase angle different from the normal spiral repeat phase of ϕ. These spin slips are a consequence of the strong basal plane anisotropy in hcp Ho, but the gain in anisotropy energy obtained by the spin slip comes at the expense of strain energy. As a consequence, the spin slips tend to be uniformly spaced. It is this ''extra'' modulation that gives rise to the unusual series of magnetic periodicities observed in incommensurate Ho at low temperature. The additional strain energy in the spin slips also leads to a characteristic lattice distortion (which produces extra charge Bragg peaks), whose periodicity is also related to that of the spin slips.[5] McMorrow *et al.*[6] have recently made an analogy between the spin slips in Ho and the unusual paramagnetic planes found in the magnetic structure of CeSb, which has the same crystal structure and planar arrangements of moments as found in UAs. It is natural to adapt these arguments to try to explain the extra modulation seen in the present experiment. Since the periodicity in reciprocal space that we observe ($k_m=0.44$) is smaller than $k=1/2$, this implies that the real space arrangement has a longer periodicity, and it is therefore natural to propose spin *additions*.

The principal commensurate magnetic structure of interest has the periodic spin arrangement $(++--++--)$. Additional spins may be inserted into this structure to form an incommensurate modulation in the commensurate phase, e.g., $(++[+]--++--[-])$; see Fig. 4. The unit cell of the spin-addition structure is constructed from two different types of spin blocks, which describe the structure in the absence and presence of the additional spin. Following the notation of Lovesey and Collins,[7] the total length of the spin addition cell, l, is therefore constructed from a number of different blocks of spins, N (normal) and S (spin addition), each containing a different number of spins, L_N and L_S, respectively, and hence

$$l=NL_N+SL_S. \tag{1}$$

(Note in Ref. 7, the S represents a spin slip whereas here it represents a spin addition.) In our model the normal spin block, L_N, $(++)$ or $(--)$, *advances* the phase of the modulation by π, and the spin addition block, L_S, $(+)$ or $(-)$ *retards* the phase by $\pi/2$. The normal spin blocks contain two spins ($L_N=2$) and the spin-addition block contains one spin ($L_S=1$), and the length of the primitive cell can be written $l=2N+S$. The number of cycles of the modulation is then

$$n=N/2-S/4. \tag{2}$$

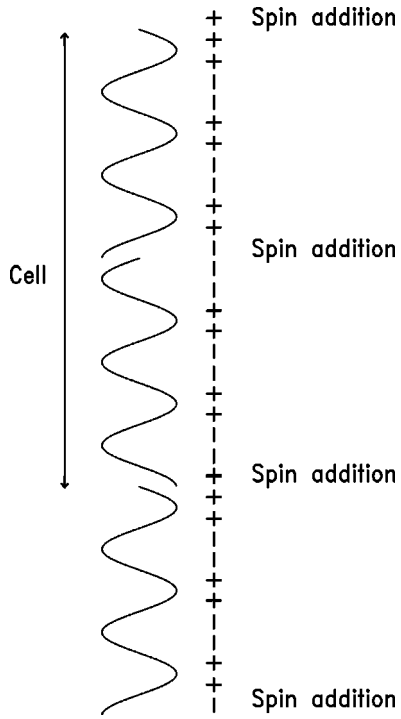

FIG. 4. An illustration of the spin addition model for the case $S=2$ and $N=10$ which results in $k_m \sim 0.41$ [Eq. (3)]. The extra spins inserted into the commensurate $++--$ structure, and the cell length, are labeled.

The wave vector of the additional magnetic modulation $k_m = p_c/p_m$, where $p_c = 2$ is the period of the charge and $p_m = l/n$ is the period of the magnetic modulation,

$$k_m = 2/(l/n) = 2n/l = (N - S/2)/l$$
$$= (l/2 - S/2 - S/2)l = 1/2 - S/l. \quad (3)$$

To conserve antiferromagnetism, S must be even. The modulation wave vector $k_m \sim 0.44$ when $S/l = 2/32$, with $S = 2$ and $N = 15$. Figure 4 illustrates the case for $S=2$ and $N=10$ in which $l=22$ and $k_m \sim 0.41$.

This model presupposes two discrete volumes of the crystal: V_1 and V_2, where $V = V_1 + V_2$. In volume V_1, which, judging by the intensity of the extra modulation, makes up 99% of the volume of the crystal, the periodicity is regular $k = 1/2$ and is essentially infinitely long-range ordered. The full-width at half-maximum (FWHM) of the magnetic peaks (see Figs. 2 and 3) are close to the instrumental resolution and that of the charge peaks, so may be taken as representing infinite order. On the other hand, the small region $V_2 \sim 0.01$ V has a periodicity that can be understood on the basis of the spin addition model. The correlation length ($\xi \propto 2/\mathrm{FWHM}$) is clearly much shorter than in the main volume V_1. The scattering volume of the extra peak is $\sim 1\%$ of the total scattering volume. The probe depth of photons at the uranium M_4 resonance is about 1000 Å, and we find that the width of the extra peak corresponds to a correlation length of approximately 200 Å.

In Fig. 5 we plot the variation of wave vector k_m with correlation length ξ, with temperature as an implicit parameter. For the $x = 0.18$ sample, the correlation length increases up to $\sim$250 Å at which point $k_m \sim 0.44$ implying $S/l \sim 2/32$ so there are 15 unit cells on average between spin additions. On further cooling (Fig. 2) the extra peak disappears for the $x = 0.18$ sample with a decrease in the correlation length. For the $x = 0.20$ sample, on the other hand, the correlation length increases with decreasing temperature until it reaches some 250 Å with a distance of also about 15 unit cells (i.e., 30 regular layers) between the spin additions.

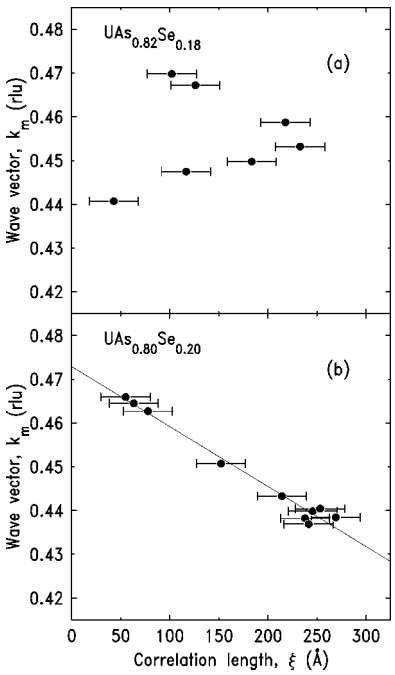

FIG. 5. The variation of the wave vector k_m versus correlation length, with temperature as an implicit parameter, for (a) $x = 0.18$ and (b) $x = 0.20$. As the temperature is lowered the correlation length increases up to about 250 Å for both samples. On further cooling the peak disappears for the $x = 0.18$ sample whereas the wave vector and correlation length remain constant for $x = 0.20$.

For the $x = 0.22$ sample, the extra peaks are very small, and we can do no more than confirm their presence, with a short correlation length.

IV. DISCUSSION

We have shown in this paper that a plausible explanation for the extra diffraction peak is that it arises from regions of the crystal in which there is an additional periodicity. This is connected to the underlying ($k = 1/2$) periodicity by the insertion of extra planes of moments. On average, the spacing between these so-called spin additions is between $\sim$100 and 200 Å, so that the ordering is relatively long range. However, the extra peaks themselves are quite broad in reciprocal space, indicating that either this periodicity is poorly defined or that the scattering volume is broken up into many smaller domains, or both. Recalling the phase diagram (Fig. 12 of paper I), we note that the place in which the new phase appears (hatched region in Fig. 12) is at the boundary (in terms of both temperature and x) between the $2\mathbf{k}$ and $3\mathbf{k}$ structures. This is seen directly in following the $0.18 \leqslant x$

$\leqslant 0.22$ samples as a function of temperature. All samples in this composition range show a tetragonal lattice distortion (see Fig. 8 of I) at about 50–60 K. At higher temperature they are $3\mathbf{k}$ and thus cubic, but at least a large part of the sample must become $2\mathbf{k}$ below 60 K. The $x=0.25$ sample does not undergo this transition and so is $3\mathbf{k}$ at all temperatures. No extra peak is found in this sample. Crystals with $x<0.18$ do not form the $3\mathbf{k}$ structure.

Of course, both $2\mathbf{k}$ and $3\mathbf{k}$ structures have the same periodicity, $k=1/2$. However, since the transformation between them, at least when their energetics are similar, may be sluggish, we suggest that the spin-addition phase exists in small interdomain regions between the volumes populated by $2\mathbf{k}$ and $3\mathbf{k}$ structures. The linear relationship between the correlation length (ξ) and wave vector (k) in Fig. 5, especially for the $x=0.2$ sample, indicates a relationship between the distance between spin additions (the fault density) and ξ. This relationship can be thought of more directly by considering the dependence of $S/l=(1/2-k_m)$, which is proportional to the fault density, on ξ. The fault density governs the periodicity of the modulation. Assuming that the correlation length is the sum of the spin addition cells, we can expect a linear relationship between the fault density and the correlation length. Moreover, for the $x=0.2$ sample, a simple extrapolation of the line in Fig. 5 gives $\xi=0$ at $k_m=0.027$ rlu, corresponding to faults every $\sim$200 Å. For a larger spacing (smaller fault density) the repulsion between faults at this distance is apparently insufficient to establish the regularity necessary to produce a diffraction peak. Similarly, we do not observe $k_m>0.060$ rlu, corresponding to fault spacings at every $\sim$90 Å. We speculate that for a larger fault density the cost in magnetic exchange energy is too great for the interfacial region to be stable.

The detailed energetics of this proposal remain to be calculated, but the adjustments necessary to accommodate both the volume discontinuity and lattice distortion, as well as the change of symmetry between the $2\mathbf{k}$ and $3\mathbf{k}$ regions, certainly provide scope for a modification of the underlying magnetic structure in the regions separating these distinct phases.

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