Resonant x-ray scattering from $UAs_{0.8}Se_{0.2}$: Multi-*k* configurations

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Using resonant x-ray scattering to perform diffraction experiments at the U M_4 edge novel reflections of the generic form $\langle kkk \rangle$ have been observed in $UAs_{0.8}Se_{0.2}$ where $\boldsymbol{k}=\langle k00 \rangle$, with $k=\frac{1}{2}$ reciprocal lattice unit, is the wave vector of the primary (magnetic) order parameter. The $\langle kkk \rangle$ reflections, with 10^{-4} of the $\langle k00 \rangle$ magnetic intensities, cannot be explained on the basis of the primary order parameter within standard scattering theory. A full experimental characterization of these reflections is presented including their polarization, energy, azimuth and temperature dependencies. On this basis, we establish that the reflections most likely arise from the electric dipole operator involving transitions between the core $3d$ and partially filled $5f$ states. The temperature dependence couples the $\langle kkk \rangle$ peak to the triple-$\boldsymbol{k}$ region of the phase diagram; below $\sim$50 K, where previous studies have suggested a transition to a double-$\boldsymbol{k}$ state, the intensity of the $\langle kkk \rangle$ is dramatically reduced. Whilst we are unable to give a definitive explanation of how these novel reflections appear, the paper concludes with a discussion of the phase diagram and raises the possibility that these reflections may be understood in terms of the coherent superposition of the three primary (magnetic) order parameters.

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I. INTRODUCTION

Since their discovery in 1963 by Kouvel and Kasper,[1] multi-$\boldsymbol{k}$ configurations have generated their share of confusion in the description of magnetic structures. The ambiguities arise since magnetic systems commonly lower their free energy by formation of domains. This eventuality frequently renders the best-known technique for their microscopic identification, neutron diffraction, impotent in the determination as to whether the magnetic structure is single-$\boldsymbol{k}$ or multi-$\boldsymbol{k}$. The respective characteristics are that a single-$\boldsymbol{k}$ configuration has only one magnetic propagation vector in any given magnetic domain whilst a multi-$\boldsymbol{k}$ configuration is defined by the *simultaneous* presence of more than one such propagation vector with intersite phase coherence. Given the possibility of multiple scattering, one immediately sees the likelihood of confusion in the interpretation of diffraction peak intensities from a multidomain sample.

Neutron diffraction is a bulk technique, sensitive to the spatial periodicities of the magnetic-field modulation. In general one cannot locate the scattering volume from which the diffraction peaks arise to a precision better than that given by the incident and scattered beams' intersection with the sample. Given incident flux limitations, even at the most powerful neutron sources, beams can rarely be made sufficiently small (on the scale of magnetic domains) to identify, unambiguously, the magnetic configuration from intensity measurements in a multidomain sample. External perturbations can, of course, change the domain populations and may allow identification, but this always begs the question as to whether the external perturbation may have changed the intrinsic magnetic configuration.

To be specific we take the case of the system $UAs_{1-x}Se_x$ where complete solid solutions exist and a considerable amount of neutron diffraction has been performed.[2] Diagrams of the possible magnetic structures for $0<x<0.3$ are shown in Fig. 1. The single-$\boldsymbol{k}$ configuration has three distinct (tetragonal) domains, as does the $2\boldsymbol{k}$ state, whilst the cubic $3\boldsymbol{k}$ phase forms in a single magnetic domain. In these illustrations the repeat distance of the magnetic structure is twice the NaCl-type chemical unit cell, so the magnitude of the wave vector of the magnetic modulation is given by $k=\frac{1}{2}$ reciprocal lattice units (rlu). The primary magnetic reflections are then of the form $\langle k00 \rangle$ where the $\langle \ldots \rangle$ indicates a permutation over indices. These reflections, which are the *only* ones observed by neutron diffraction, are also imaged by resonant x-ray scattering (RXS), via the $F^{(1)}$ electric dipole ($E1$) scattering amplitude.[3,4] In addition, the RXS cross section exhibits $F^{(2)}$ dipole amplitudes,[5,6] which give rise to peaks at positions of the form $\langle kk0 \rangle$. The symmetries of the $F^{(1)}$ and $F^{(2)}$ terms may be exploited to distinguish, respectively, between single-$\boldsymbol{k}$ and multi-$\boldsymbol{k}$ structures.[7]

Under the constraints of the geometric structure factor, the $F^{(2)}$ amplitude projects, on a given scattering center, a *pair* of the $\langle k00 \rangle$ order parameters which, given intersite phase coherence, yields Bragg diffraction peaks of the form $\langle kk0 \rangle$. The respective $F^{(1)}$, $F^{(2)}$ assignments have been experimentally verified through the polarization and azimuthal dependence of the scattered photons.[7] Moreover, even though both amplitudes are electric dipole in origin, the contributions from the $F^{(2)}$ uranium scattering amplitudes have different matrix elements and are distinguished by their resonant energy and line shape from the $F^{(1)}$ profiles.[7–9]

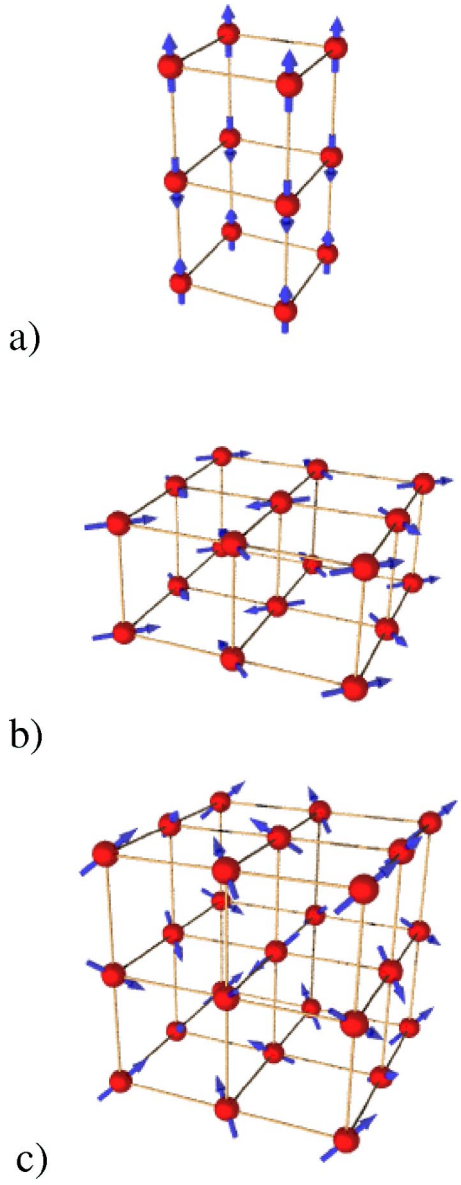

FIG. 1. $UAs_{1-x}Se_x$ crystallizes in the fcc NaCl structure. The magnetic modulation wave vector is $\langle k00 \rangle$ where $\langle \ldots \rangle$ signifies all permutations of k, and in the $x=0.2$ composition discussed here $k=\frac{1}{2}$. The magnetic moments of the four uranium atoms within the chemical unit cell have the same direction and magnitude. For simplicity we have therefore shown only the magnetic moment in the corner of each chemical unit cell. (a) In a longitudinal single-$\boldsymbol{k}$ structure with $\boldsymbol{k}=[001/2]$, the moments are aligned along [001] and the unit cell is doubled along this direction. (b) In the $2\boldsymbol{k}$ structure with $k_a=[100]$ and $k_b=[010]$, the net moment is along [110], and the unit cell is doubled in the a and b directions. (c) In the $3\boldsymbol{k}$ structure the unit cell is doubled in all directions and the net moment direction is [111]. Of all the structures $3\boldsymbol{k}$ is the only one in which a unique phase domain exists.

In the course of these experiments an additional group of reflections, much weaker than the other two sets described above, of the generic form $\langle kkk \rangle$ have been observed. In this paper we give details characterizing these reflections and our difficulty in explaining them within conventional scattering theory.

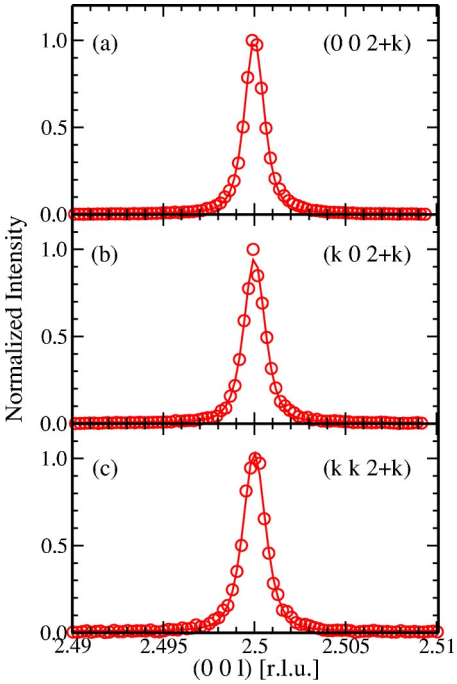

FIG. 2. Scans along the [001] direction of the reflections (0 0 5/2), (1/2 0 5/2), and (1/2 1/2 5/2) [top, middle, and bottom panels, respectively]. Solid lines are a fit to a Lorentzian squared line shape. The half width at half maximum as determined by fitting was found to equal 6.96×10^{-4}, 7.54×10^{-4}, and 8.03×10^{-4} rlu for the (0 0 5/2), (1/2 0 5/2), and (1/2 1/2 5/2), respectively. The data were taken at a temperature of 60 K.

II. EXPERIMENTAL DETAILS AND RESULTS

Experiments were performed with σ incident polarization of the photon beam at the ID20 beamline,[10] ESRF, Grenoble, France in the configuration used in previous work.[7] The studies were carried out on a single crystal of $UAs_{0.8}Se_{0.2}$ which, above a tetragonal distortion at $T^*\sim50$ K, exhibits the cubic rock salt structure.[3] On further warming, $UAs_{0.8}Se_{0.2}$ is known to pass from a magnetic configuration of commensurate ($k=\frac{1}{2}$) to incommensurate ($k=0.475$) wave vector at $T_0\sim119$ K, and to the paramagnetic state at $T_N\sim124$ K.[2–4] It has been shown, using a combination of both neutron and x-ray techniques,[2,7] to adopt a multi-$\boldsymbol{k}$ structure for $T<124$ K.

Representative reflections for the $\langle k00 \rangle$, $\langle kk0 \rangle$, and $\langle kkk \rangle$ peaks are illustrated in Fig. 2, where scans taken along the [001] direction are shown. These data were taken with a high resolution Ge (111) analyzer and their sharp width is indicative of long-range order. Figure 3 displays the dependence on incident photon energy of the scattered intensity at the positions (0 0 5/2), (1/2 0 5/2), and (1/2 1/2 5/2) for both the $\sigma\rightarrow\sigma$ and $\sigma\rightarrow\pi$ channels of the cross section at 70 K. As Fig. 3 shows, the (1/2 1/2 5/2) peak appears *only* in the $\sigma\rightarrow\pi$ channel with a resonant energy and width comparable to that of the (0 0 5/2), evidence which already suggests that the $\langle kkk \rangle$ peak may arise from the $F^{(1)}$ dipole ($E1$) amplitude.

Figure 4 shows the azimuthal dependence of the intensity of the $\langle kkk \rangle$ reflections (1/2 1/2 5/2) and (–1/2 1/2 5/2) in

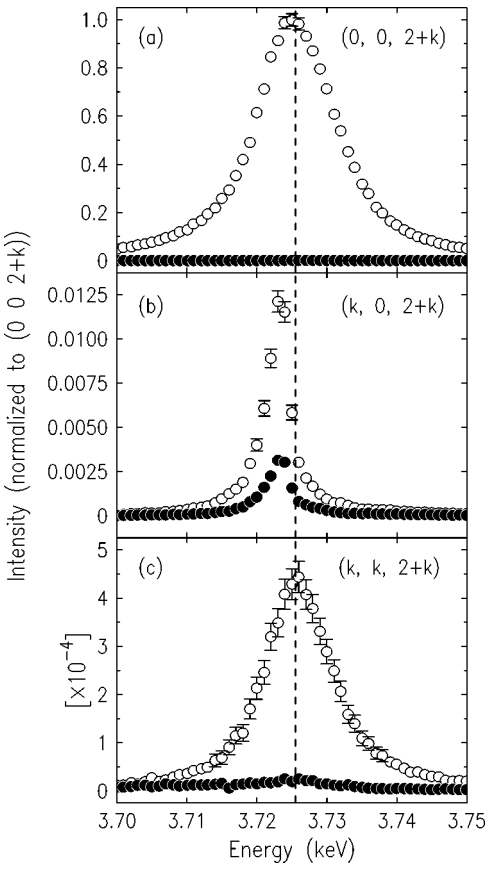

FIG. 3. Scans of the incident photon energy with polarization analysis of the scattered beam for $\boldsymbol{k}$, $2\boldsymbol{k}$, and $3\boldsymbol{k}$ reflections measured in a single crystal of $UAs_{0.8}Se_{0.2}$ in the vicinity of the U M_4 resonance which is marked with a dashed vertical line. The temperature was 70 K for all panels and the wave vector is $k=\frac{1}{2}$. The incident polarization is σ, and using a Au (111) analyzer the open (closed) points correspond to intensity in the scattered π (σ) channel. (a) The $\langle k00\rangle$ reflection (0 0 5/2) which is also observed in neutron diffraction. Note that it occurs only in the rotated $\sigma\rightarrow\pi$ channel. (b) The reflection (1/2 0 5/2), of the form $\langle kk0\rangle$, arises from the noncollinear $2\boldsymbol{k}$ magnetic structure and is discussed in detail in Ref. 7. Note that contributions occur in both polarization channels, the energy maximum is shifted and the resonant energy peaks are narrow. (c) The novel $\langle kkk\rangle$ type of reflection, (1/2 1/2 5/2), discussed in this paper. Intensity only occurs in the $\sigma\rightarrow\pi$ channel at all azimuths with an energy position and width similar to case (a) above.

the $\sigma\rightarrow\pi$ channel. The smooth variation of the intensity eliminates multiple scattering as a possible source of these peaks. The lines are calculated from the $F^{(1)}$ term of the $E1$ cross section, assuming a symmetry-breaking vector parallel to the reduced wave vector $\langle kkk\rangle$, i.e., along [1 1 1] for (1/2 1/2 5/2) and along [−1 1 1] for (−1/2 1/2 5/2). This appears to eliminate the magnetic moment as the relevant symmetry-breaking vector. These aspects are discussed further below.

The temperature dependencies of the (1/2 0 2), (1/2 1/2 2), and (1/2 1/2 5/2) peaks are given in Fig. 5. The (0 0 5/2) reflection represents one primary order parameter whilst the $2\boldsymbol{k}$ (1/2 1/2 2) reflection involves two simultaneously present

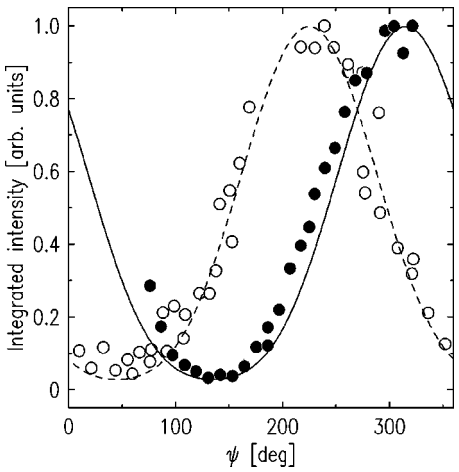

FIG. 4. Azimuthal scans in the $\sigma\rightarrow\pi$ channel about the scattering vector for the (1/2 1/2 5/2) (open points) and (−1/2 1/2 5/2) (closed points) reflections. The lines correspond to the analyzis described in the text. Note that for all azimuthal angles the intensity in the $\sigma\rightarrow\sigma$ channel is zero.

at each scattering center and propagating with a fixed phase relationship.[7] The temperature dependencies of $I_{\langle k00\rangle}$, $I_{\langle kk0\rangle}$, and $I_{\langle kkk\rangle}$ for 70 K$<T<$117 K in Fig. 5 lie approximately in the ratio $I^{0.4}$:I:$I^{1.5}$.

Detailed specific heat and magnetization measurements were made using the sample used in the diffraction experiments at the User Facility, Institute for Transuranium Elements, Karlsruhe.[11] The specific heat was measured by the relaxation method in a Quantum Design PPMS-9 calorimeter over the temperature range 4.2–300 K and magnetic fields up to a maximum of 9 T. The magnetization measurements were carried out using a Quantum Design SQUID magnetometer (MPMS-7) in applied magnetic fields up to 7 T.

We show in Fig. 6 the results of (a) the integrated intensity of the (1/2 1/2 5/2) peak, (b) heat capacity at zero field, and (c) the susceptibility in a magnetic field of 0.1 T, as a function of temperature. The loss of intensity observed in the $\langle kkk\rangle$ reflection is coupled to the nominal $2\boldsymbol{k}\Leftrightarrow 3\boldsymbol{k}$ transition[3,4] as seen in both specific heat and susceptibility at T^*.

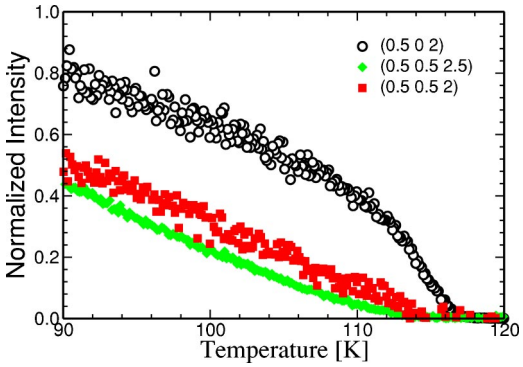

FIG. 5. Peak intensity of the $\langle k00\rangle$, $\langle kk0\rangle$, and $\langle kkk\rangle$ (circles, squares, and diamonds, respectively) as a function of temperature near $T_0=119$ K.

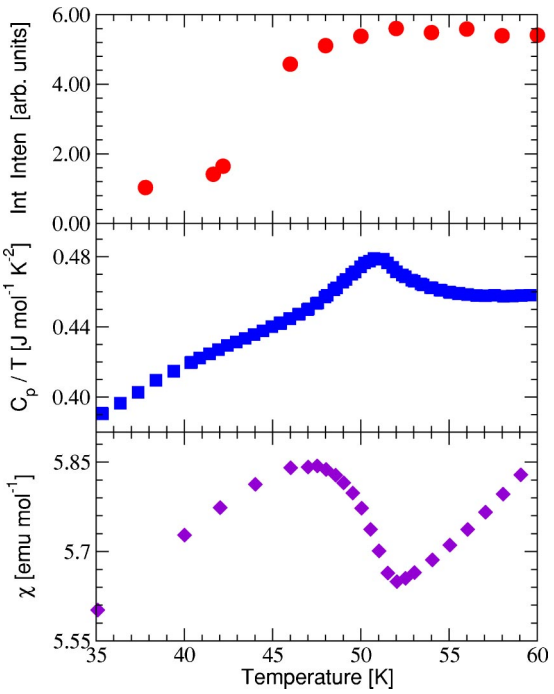

FIG. 6. Integrated intensity of the (1/2 1/2 5/2) reflection in the region 35 K$<T<$60 K (top panel), linear coefficient of the heat capacity in zero applied magnetic field (middle panel) and magnetic susceptibility in a applied magnetic field of 0.1 T (bottom panel).

III. DISCUSSION

Before turning to possible explanations of the $\langle kkk\rangle$ peaks, we recapitulate the phase diagram of the $UAs_{0.8}Se_{0.2}$ as suggested by earlier neutron[2] and RXS experiments.[3,4] First, the disappearing intensity of the $\langle kkk\rangle$ peaks and the presence of a lattice distortion below $T^*\sim 50$ K,[3,4] show that the low-temperature state is most likely a $2\boldsymbol{k}$ phase.[2] Above T^*, high-resolution x-ray experiments have not been able to detect any distortion from cubic symmetry. This suggests, in agreement with the neutron results, that the sample is not in a simple $2\boldsymbol{k}$ (or single-$\boldsymbol{k}$) phase. Previous authors have suggested this to be a $3\boldsymbol{k}$ state.[2]

We now examine possible origins of the $\langle kkk\rangle$ peaks. A simple explanation would be that at the level of 10^{-4} of the total volume there are regions that exhibit an ordering with the single-$\boldsymbol{k}$ wave vector $\langle 1/2\ 1/2\ 1/2\rangle$. This would explain the observed energy dependence of the scattering, Fig. 3. However, there are a number of observations which contradict such a scenario. First, the similar, sharp, $\boldsymbol{q}$ widths of $\langle k00\rangle$, $\langle kk0\rangle$, and $\langle kkk\rangle$ reflections (Fig. 2) are indicative that the $\langle kkk\rangle$ peaks represent (bulk) long-range order. Second, the simple relation of their temperature dependencies to the $\langle k00\rangle$ and $\langle kk0\rangle$ peaks for $T^*<T<T_0$, which strongly suggests scattering amplitudes proportional to the first, second, and third powers of the primary order parameters (Fig. 5), would then have to be completely fortuitous which is hard to accept. Third, the calculation of the relative azimuthal dependence of the (1/2 1/2 5/2) and (−1/2 1/2 5/2) peaks appears to eliminate any sources of conventional single-$\boldsymbol{k}$ magnetic scattering. Moreover, single-$\boldsymbol{k}$ (1/2 1/2 1/2) ordering has, to date, never been reported in NaCl-structure uranium compounds. These observations all suggest that the $\langle kkk\rangle$ reflections are not a product of local chemical or structural disorder but rather are intimately related to the primary long-range order parameters of the material.

As already noted, both the electric dipole cross section and the geometric structure factor of the magnetic moment for $\boldsymbol{Q}=\langle kkk\rangle$ vanish. The lowest combination of order parameters with finite geometrical structure factors is of rank 3, i.e., of the form $M_xM_yM_z$. For example, a symmetrized, octupolar operator couples directly to the $F^{(3)}$ term of the $E2$ cross section,[6] as observed, e.g., in V_2O_3.[12,13] To date however, there is no evidence of any $E2$ resonances at the actinide $M_{4,5}$ edges, since these would couple to the g states with a correspondingly small matrix element. Furthermore, the $E2$ cross section would give rise to scattering in both the $\sigma\rightarrow\sigma$ and $\sigma\rightarrow\pi$ polarization channels, and one would expect the maximum of the resonance to be shifted towards the pre-edge region, as observed in transition metal[12] and rare-earth systems.[14,15] Rather, the energy and polarization profiles link these reflections to the $F^{(1)}$ term of the $E1$ cross section.

The effective symmetry-breaking direction lies along the reduced wave vector $\langle 111\rangle$, as indicated by analysis of the azimuthal dependencies shown in Fig. 4. Any combined lattice distortion or charge density wave (CDW) at $\langle kk0\rangle$ with a magnetic dipole $\langle k00\rangle$ construction is not supported by our observations. Furthermore, there is no experimental evidence for either a distortion or CDW in the cubic phase for such hypothetical constructions.[16]

A mechanism to couple an $E1$ resonance to the octupolar moment of the valence shell was recently suggested by Lovesey *et al.*[9] They found that the $E1$-$F^{(2)}$ (rank-2 tensor) term in the cross section observed in NpO_2 may be constructed from a magnetic octupole (rank 3) and an induced Zeeman splitting in the $3d$ core shell (rank 1). The product of these tensors contains one of rank 2 which may have been observed in the x-ray experiment.[8] Extending this framework, coupling a rank (R) and rank ($R+1$) tensor will yield a vector (rank 1) in its product with a $\langle kkk\rangle$ scattering amplitude. Hypothetical examples include combining a $\langle k00\rangle$ magnetic moment in the $5f$ valence level with a $\langle kk0\rangle$ quadrupolar splitting of the $3d$ core levels or vice versa. A still more complex scenario would be a $M_xM_yM_z$ octupolar moment in the $5f$ shell (rank 3) with a rank 2 quadrupolar splitting of the $3d$ core levels. What physical field would give the required core-level anisotropy is unknown and such mechanisms are currently without foundations.

We conclude with a comment on the phase diagram. We confirm the low-temperature (tetragonal) configuration to be a state of $2\boldsymbol{k}$ domains composed of phase-coherent pairs of the primary order parameters, in agreement with inferences made in earlier work.[2–4] As the temperature is raised, the tetragonal $2\boldsymbol{k}$ phase melts with fluctuations of increasing frequency between the possible domains giving, above T^*, a state which maintains a cubic environment within which both $2\boldsymbol{k}$ and $3\boldsymbol{k}$ correlations of the primary order parameters coexist. Due to the absence of any measurable tetragonal

distortion it was previously suggested that the phase between T^* and T_O is a $3\boldsymbol{k}$ state. However, there is no direct evidence for this assumption. In fact unpublished field-dependent specific-heat measurements, as well as other results are rather difficult to interpret on this basis. Thus, the nature of the phase for $T^*<T<T_O$ remains unclear. At present we have no direct evidence on the lifetime of either $2\boldsymbol{k}$ or $3\boldsymbol{k}$ correlations above T^*. The rapid nature of the RXS technique (temporal resolution of $\sim 10^{-15}$ s) may be of importance to the observations if the relevant coherence times are on the scale of the inverse bandwidth.

On the basis of the wave vector, incident photon energy, polarization, azimuth and temperature dependencies, this paper eliminates many of the possible explanations for the presence of the $\langle kkk \rangle$ reflections, however, more work is needed to explain their observation even at the *qualitative* level.[17] We hope the observations and discussion presented will stimulate further experiments and theoretical studies in this and other multi-$\boldsymbol{k}$ systems.

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