Experimental report

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Proposal: 5-31-2656 **Council:** 10/2018

Title: Crystal and magnetic structures investigation on antiferromagnetic spintronic material - tetragonal Cu1+xMn1-xAs

Research area: Physics

This proposal is a new proposal

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Samples: CuMnAs

Instrument	Requested days	Allocated days	From	To
D20	3	3	12/07/2019	15/07/2019

Abstract:

The development of antiferromagnetic spintronics is still in its infancy but thin-film CuMnAs has already received much interest due to its high Néel temperature (TN~480 K) and the ability to reorient the magnetic moments using current pulses. Specific symmetry properties of the tetragonal polymorph make it the most interesting for spintronic applications but due to a lack of high quality bulk samples, studies have been limited to thin films. Our recent synthesis efforts have now afforded bulk samples of the tetragonal phase, with a range of compositions in the series Cu1+xMn1-xAs. We have found that stoichiometry changes tune the Néel temperature as well as crystallographic and magnetic structure of Cu1+xMn1-xAs (significantly). We propose to use powder neutron diffraction with the D20 diffractometer to perform high quality refinements of both across this series of compositions.

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Crystal and magnetic structures investigation on antiferromagnetic spintronic material - tetragonal $Cu_{1+x}Mn_{1-x}As$

Background and justification

Antiferromagnetic materials are currently being investigated for use in the next generation of spintronic storage devices and due to specific symmetry conditions present in CuMnAs (the antiferromagnetic sublattices form inversion partners on a centrosymmetric crystal lattice) electric currents can be used to reorient the spins – writing to antiferromagnetic memory [1].

Until recently, bulk synthesis of CuMnAs found an orthorhombic structure (space-group *Pnma*) with a Néel temperature of T_N = 330-360 K [2,3], however thin film studies invariably find a tetragonal structure (space-group *P4/nmm*) with a significantly higher Néel temperature of T_N = 480 K [4,5]. It is this tetragonal structure that fulfils the symmetry requirements for current-induced spin-reorientation and as such holds particular interest for spintronic applications. We recently prepared tetragonal $Cu_{1+x}Mn_{1-x}As$ (x = 0 – 0.5) and showed that the Néel temperature can be tuned almost linearly from T_N~500 K to 350 K by increasing x from 0 to 0.5 [6] This experiment had three goals: to confirm the structure of bulk CuMnAs, where refinement of atomic site occupations is difficult using X-rays due to similar atomic numbers (Z = 29, 25 and 33, for Cu, Mn and As, respectively); to confirm the magnetic structure put forward by thin-film neutron diffraction studies; and to elucidate the structural changes important to the tuning of the Neel temperature through the substitution series.

Experimental protocol

During the four-day measurement on D20, using the cryofurnace sample environment, we measured the temperature dependent diffraction profiles of four members of the $Cu_{1+x}Mn_{1-x}As$ series, with x = 0.02, 0.15, 0.30 and 0.45.

The crushed polycrystalline samples with masses ranging from 3.08 – 8.65 g, prepared by solid state synthesis and previously checked by X-ray diffraction and magnetisation measurements, were loaded into vanadium cans (Ø = 6 and 7 mm) with a split sealing ring to allow He gas exchange with the sample environment, preventing oxidation at high temperature.

The following collection protocol was used for the samples with x = 0.02, 0.15 and 0.3:

Once inserted at 300 K, the sample was rapidly heated to the cryofurnace maximum temperature (stabilising at 535 K). During this *initial heating*, fixed-detector diffraction patterns were collected to check sample integrity (λ = 2.41 Å). Once thermalized at 535 K, a high-statistics detector-scan measurement (λ = 2.41 Å and 1.54 Å) in the paramagnetic state was collected. The sample was then cooled at a constant rate (1 – 2 K/min) whilst collecting (fixed-detector, λ = 2.41 Å), with *cooling ramp* measurement time corresponding to ~5 K thermal steps. At base temperature (~1.6 K) another high-statistics detector-scan diffraction pattern was collected (λ = 2.41 Å and 1.54 Å). The samples were then heated and stabilised at several temperatures for additional high-statistics measurements (typically 100, 200, 300 and 400 K), before returning to 300 K for sample change.

The measurements of the x = 0.45 sample differ only in that an additional high-statistics data set was collected on sample insertion at 300 K, as well as a controlled heating ramp with measurements during the *initial heating* to the maximum temperature.

Results

Sample 1: $Cu_{1.02}Mn_{0.98}As$ (x = 0.02)

Preliminary measurements during the initial heating agreed with the expected pattern. During the rapid heating, several low-Q peaks rapidly decreased in intensity before disappearing, suggesting a magnetic origin.

The high statistics data set can be reasonably fitted by the expected structure *P4/nmm* (fig. 1a), although there are some minor *hkl*-dependent peak positional offsets as well as some intensity mismatch. It is not yet clear if these are extrinsic (perhaps due to sample offset from the diffractometer center as well as some preferred orientation) or intrinsic features (evidence of a true lower-symmetry structure).

During cooling below the T_C = 520 K, an additional set of magnetic reflection appear and rapidly gain intensity at the expense of the paramagnetic background scattering. These reflections can be well indexed and fit by the previously proposed magnetic structure (*Pm'mn*, [4]). Preliminary temperature dependent refinements show an anomalous temperature dependence of the c-axis on cooling, initially expanding before typical thermal contraction occurs (fig. 1b. The refined Mn-site moment initially increases and saturates at a value of ~2.65 μ_B/Mn, although two anomalies are present in the temperature dependence of the moment (fig. 1c), the first of which is concominant with the maximum of the *c*-axis lattice parameter. These anomalies could indicate a subtle nuclear or magnetic structural transition although further analysis is required.

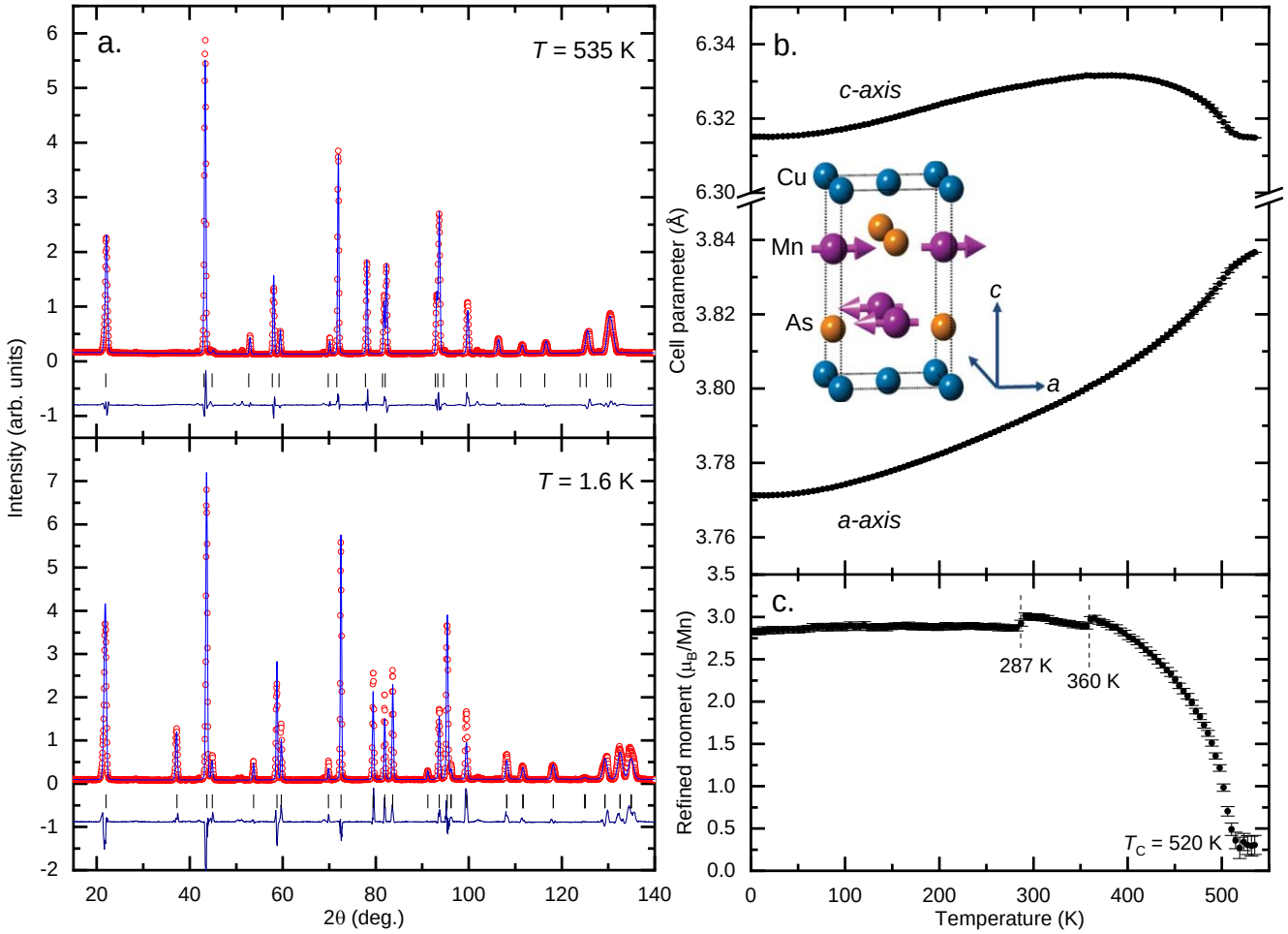

Figure 1 Refinement results for $Cu_{1.02}Mn_{0.98}As$. a. High temperature paramagnetic structure, and low-temperature ferromagnetically ordered structure, upper and lower, respectively. b. Cell parameter evolution with temperature. The refined nuclear and magnetic structure shown in the inset. c. Temperature dependence of the refined moment, with characteristic temperatures indicated.

Sample 2: $Cu_{1.15}Mn_{0.85}As$ (x = 0.15)

As with sample 1, the high temperature structure of sample 2 can be well fit by the previously proposed model. Cooling results, again, in magnetic reflections appearing at positions consistent with the proposed magnetic structure below T_C = 450 K, although refinements to confirm the finer details of the ordering are still underway.

Sample 3: $Cu_{1.30}Mn_{0.70}As$ (x = 0.30)

Unlike samples 1 and 2, the data collected on initial heating for sample 3 did not match that expected – with both magnetic and nuclear peaks not indexed by the expected tetragonal structure. Due to the rapid-heating protocol used, this data is not suitable for convincing structural identification of this unknown room-temperature phase. Whilst heating, the magnetic reflections subsided and a structural transformation took place that resulted in high statistics data at 535 K that can be fitted by the *P4/nmm*.

The structural transformation observed on heating was, however, not observed on cooling. Instead, peaks consistent with the high-temperature tetragonal *P4/nmm* structure are apparent on cooling to base temperature. Consistent with the measured magnetization data, reflections from the magnetic phase appear at T_C 370 = K. On close inspection, additional broad diffuse scattering peaks also become apparent on cooling, suggesting the build up of additional short-range correlations in either nuclear or magnetic structure (fig. 2a). The observed behavior can be explained by a slow transition at or above room temperature that was not able to occur during this fast cooling ramp – instead trapping the high-temperature structure. The same was likely true before our lab x-ray data collection, but where the sample was left for an extended period, transformation was able to occur. Time dependent studies using our lab diffractometer are now underway.

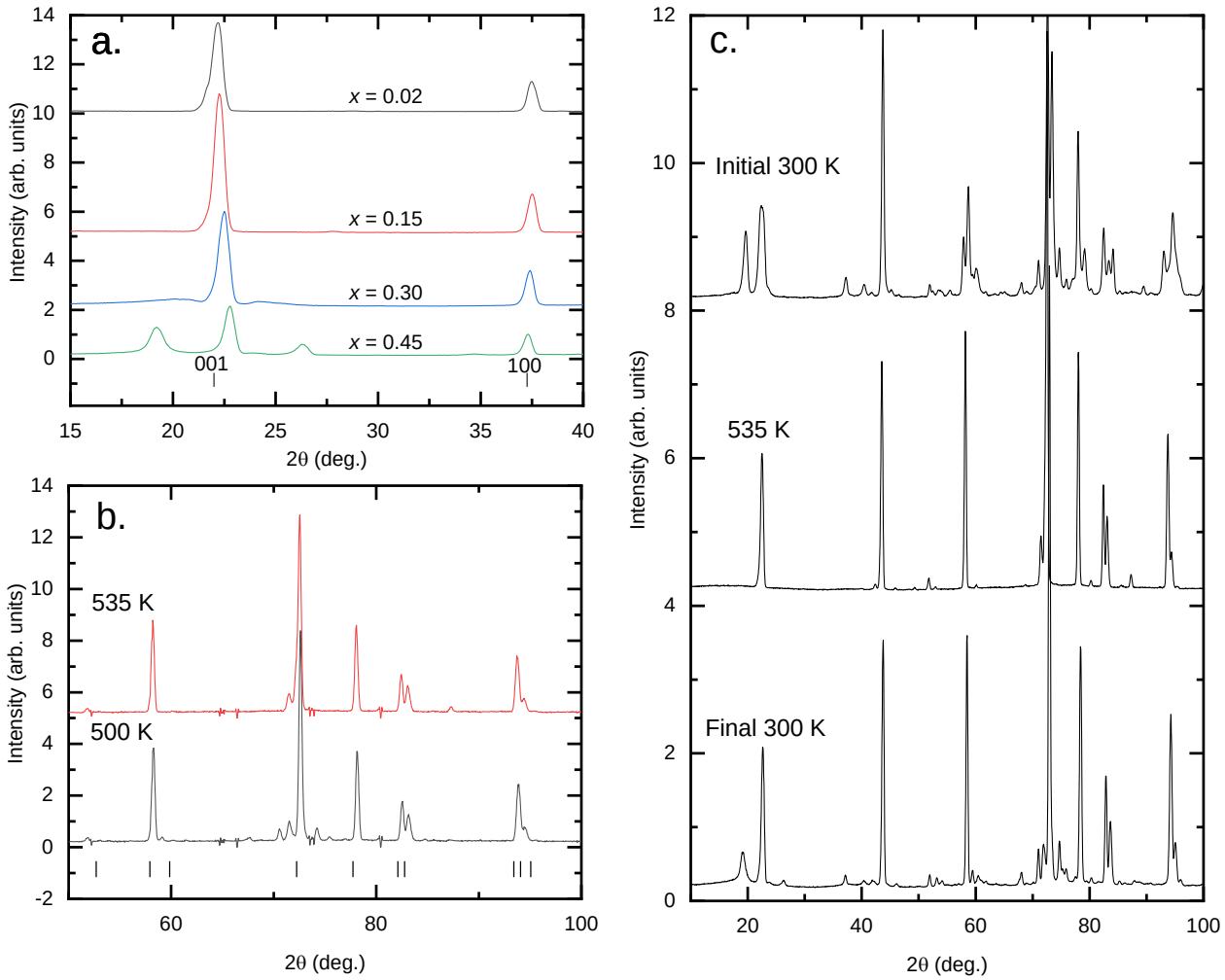

Figure 2a. Low-angle nuclear and magnetic reflections of all samples at 1.6 K. Additional diffuse scattering is observed in the x=0.30 sample, with new un-indexed peaks in the x=0.45 sample. b. Highlighting the additional structural modulation peaks that appear on cooling from 535 K to 500 K in x=0.45, tick marks represent the previously reported P4/nmm structure. c. Diffraction patterns from x=0.45 on initially inserting into the diffractometer, then on heating to 545 K, and finally after cooling to base and returning to 300 K, showing the incomplete conversion during the initial cooling, to an unknown low-temperature structure.

Sample 4: $Cu_{1.45}Mn_{0.55}As$ (x = 0.45)

As with sample 3, a different structure not previously identified is observed initially at 300 K, identifiable due to additional peak splitting and magnetic reflections. The more controlled heating protocol used for sample 4 allows us to track the transformation of this structure into the tetragonal *P4/nmm* high-temperature phase – observed at 535 K. On cooling from 535 K, superstructure peaks initially appear below 505 K (fig. 1b) that signify an unknown structural modulation – efforts to index this modulation are in progress. On further cooling, magnetic reflections appear at T_C = 304 K and are concomitant with additional splitting of several nuclear structural reflections. Possibly due to the relatively fast cooling ramp rate, this transition is again incomplete, and so at low temperature the pattern appears to consist of contributions from both the pre- and post-transformed nuclear structures, as well as presumably magnetic contributions from both phases. This is most clearly evident when considering the patterns at 300 K on initial sample insertion, and then at the end of the measurement after heating, cooling, and then returning to 300 K. Data from the virgin sample, having spent an extended period at room-temperature where the slow transformation can proceed to (near-)completion, is the most useful for identifying the low-symmetry structure but the magnetic contribution is hampering structure solution. Complementary laboratory X-ray diffraction experiments are underway to resolve this issue.

References

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