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Coupling of structure to magnetic and superconducting orders in quasi-one-dimensional $\text{K}_2\text{Cr}_3\text{As}_3$

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Quasi-one-dimensional $A_2\text{Cr}_3\text{As}_3$ (with $A = \text{K}, \text{Cs}, \text{Rb}$) is an intriguing new family of superconductors which exhibit many similar features to the cuprate and iron-based unconventional superconductor families. Yet in contrast to these systems, no charge or magnetic ordering has been observed which could provide the electronic correlations presumed necessary for an unconventional superconducting pairing mechanism - an absence which defies predictions of first principles models. We report the results of neutron scattering experiments on polycrystalline $\text{K}_2\text{Cr}_3\text{As}_3$ ($T_c \sim 7\text{K}$) which probed the low temperature dynamics near T_c . Neutron diffraction data evidence a subtle response of the nuclear lattice to the onset of superconductivity while inelastic scattering reveals a highly dispersive column of intensity at the commensurate wavevector $q = (00\frac{1}{2})$ which loses intensity beneath T_c - indicative of short-range magnetic fluctuations. Using linear spin-wave theory we model the observed scattering and suggest a possible structure to the short-range magnetic order. These observations suggest that $\text{K}_2\text{Cr}_3\text{As}_3$ is in close proximity to a magnetic instability and that the incipient magnetic order both couples strongly to the lattice and competes with superconductivity - in direct analogy with the iron-based superconductors.

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Understanding how superconductivity arises from myriad competing ground states and exotic phenomena such as quantum criticality has been an overarching theme in the study of unconventional superconductors — particularly in the well-studied quasi-two-dimensional (Q2D) cuprate and iron-based (FBS) families¹. Recently, a new family of superconducting quasi-one-dimensional (Q1D) $A_2\text{Cr}_3\text{As}_3$ (233) materials (with $A = \text{K}, \text{Cs}, \text{Rb}$) have proven fertile grounds for applying this general narrative to another system which has further lowered-dimensionality^{2,3}.

The 233 family orders in non-centrosymmetric hexagonal $P\bar{6}m2$ space group symmetry with a structural motif of double-walled sub-nano tubes (DWS) coaxial to the c -axis and of $[(\text{Cr}_3\text{As}_3)^{-2}]_\infty$ stoichiometry (see Fig. 1(e-f)) with the A -site ion acting as a spacer/charge reservoir ‘layer’^{2,4,5}. DFT calculations predict a Fermi surface built of complex mixtures of the Cr $3d$ shells with strong Q1D character^{3,6,7}. Consequently, predictions of Tomonaga-Luttinger liquid (TLL)/general non-Fermi-liquid physics, Peierls distortions, ferromagnetic (FM) fluctuations/magnetic ordering and spin-triplet superconductivity have arisen creating a sea of possible ground states and interactions out of which superconductivity stabilizes.^{3,5,7–10}

Experimentally a similarly complex picture has emerged. Non-Fermi-liquid behaviors are observed in transport, nuclear magnetic resonance (NMR) and muon spectroscopy (μSR) measurements, which indicate significant electron correlations and strong magnetic fluctuations^{11–13}. More exotically, measurements of the penetration depth find nodes in the superconducting gap while those of the upper critical field it to be highly anisotropic, greatly exceed the Pauli-pair-breaking limit,

exhibit an in-plane angular dependence and even a possible Fulde-Feerel-Larkin-Ovchinnikov state^{14–16}. Furthermore, recent angle-resolved photoemission spectroscopy reports find linear behavior of the spectral intensity near the FS indicating possible Tomonaga-Luttinger liquid type physics¹⁷. Yet these findings have found divergent explanations ranging from unconventional superconductivity with spin-triplet or singlet pairing to conventional phonon driven scenarios^{14,18,19}. This ambiguity arises partially from a lack of direct measurements determining the relevant low temperature orders. Here we investigate the structure and magnetic behavior of $\text{K}_2\text{Cr}_3\text{As}_3$ at low temperatures using neutron scattering techniques.

Synthesis of polycrystalline $\text{K}_2\text{Cr}_3\text{As}_3$ was adopted from References 11 and 4 (as detailed in the supplemental material)²⁰. Neutron powder diffraction (NPD) data were collected using the HB-2A powder diffractometer at the High Flux Isotope Reactor (HFIR) of Oak Ridge National Laboratory (ORNL) using wavelengths (λ) of 1.54 and 2.41 Å. High resolution synchrotron x-ray data were collected at beamline 11BM-B of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL) with $\lambda = 0.414$ Å. Detailed structural analyses were performed using the Rietveld method as implemented in the FullProf, GSAS and EXPGUI software suites^{21–24}. Inelastic neutron scattering experiments were carried out on HFIR’s triple-axis spectrometer HB-3. Tight collimation was used with a fixed analyzer energy of 14.7 meV.

Our analysis of both the high resolution XRD and NPD patterns found models of $\text{K}_2\text{Cr}_3\text{As}_3$ exhibiting the hexagonal space group symmetry $P\bar{6}m2$ to produce the highest quality fits in accord with previous reports (see SM for details)¹¹. Considering our room temperature refinements the crystallographic data agree with those

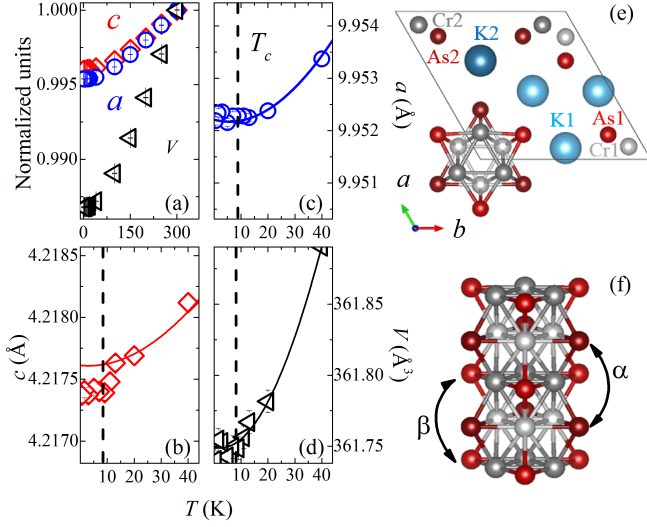


FIG. 1. Temperature dependence of $K_2Cr_3As_3$ lattice parameters a , c and unit cell volume V extracted from Rietveld refinements of the NPD patterns normalized to 300K values (a). Low temperature behavior of a , c and V (b-d). Polynomial fits to the high temperature data ($20K < T < 300K$) are plotted as guides to the eye. All y -axis ranges show the same relative percent change of the parameters. The crystal structure of $K_2Cr_3As_3$ seen along the c -axis (e) and the structure of the DWS with angles As2-Cr2-As2 and As1-Cr1-As1 denoted by α and β respectively (f). In panels (a - d) the error bars are smaller than the individual data point markers

reported in Ref 11.

Upon decreasing temperature from 300K to 0.5 K a , c and V monotonically contract (Fig. 1). For temperatures $T > 40$ K a linear thermal expansion is observed (with nearly negligible change for $T < 40$ K) with no evidence of a structural response which might arise from nuclear or magnetic orderings in contrast to DFT calculations' predictions but in accord with featureless transport data^{6,7,11}. While it is possible that the relatively large steps in temperature between 300 K and 20 K might miss a subtle lattice response, such as that commonly reported for the FBS, comparisons of the high temperature and low temperature patterns do not reveal the presence of new peaks, peak splitting or other evidence of a phase transition (see SM)²⁵⁻²⁷.

Such structural stability, despite a predicted Peierls instability, has also been observed in the Q1D chevel family ($Tl_2Mo_6Se_6$) which share the DWS structural motif^{28,29}. In these materials the DWS sublattice was found to be rigid due to the significant metal-metal bonding and unique geometry of the DWS. By analogue, we suggest the significant inter and intra Cr triangle bonding confounds the expected Peierls distortion which cannot easily lower simultaneously the energies of the inter and intra triangle bonds^{7,29}.

Considering the lattice parameters in the range of linear thermal expansion, the coefficient of thermal expansion can be obtained via the expression $\alpha = 1/V_0(V_0 -$

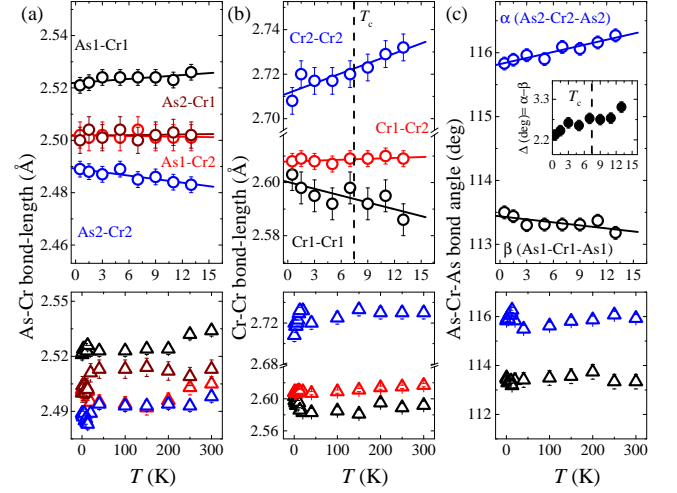


FIG. 2. Temperature dependence of $K_2Cr_3As_3$ As-Cr (a), Cr-Cr (b) and As-Cr-As (c) bond lengths and angle as determined from Rietveld refinements. The upper panels focus on $T < 20$ K while the lower panels show all measured temperatures. Inset of panel (d) shows the degree of non-centrosymmetry as measured by the difference of the two As-Cr-As angles. All scales have been configured to cover similar ranges in percent change of the plotted parameter. Linear fits are provided as guides to the eye.

$V)/(T_0 - T)$ (where V can be a or c) which finds α for a , c and V as 1.9×10^{-5} , 1.7×10^{-5} and 5.5×10^{-5} K⁻¹, respectively. The expansion along the a axis is slightly larger than along c as might be expected from the highly anisotropic quasi-1D nuclear structure. This is in accord with reports on $Rb_2Cr_3As_3$ and $Cs_2Cr_3As_3$ as well as pressure studies both of which found the a -axis more sensitive to external and chemical pressure^{4,5,30,31}. These values of α are similar to the relatively high values reported for paramagnetic (PM) states of the 11 and various 122 members of the FBS family where strong spin-fluctuations are thought to contribute to the thermal expansion³²⁻³⁹. As we will show similar spin-fluctuations exist in $K_2Cr_3As_3$ and may be responsible for the large α values.

While no clear signature of a structural phase transition exists, close inspection of the low temperature behavior ($0.5 \text{ K} \leq T \leq 20 \text{ K}$) of the c -axis reveals a response of the lattice near $T_c \sim 7 \text{ K}$ (Fig. 1(b)). In this range, the c -axis exhibits a contraction just before T_c upon cooling while the a -axis remains constant. V undergoes a commensurate contraction reflecting the reduced c -axis (Fig. 1(b-d)). The effect is anisotropic being observed only in the ostensibly stiffer c -axis and appears to correspond to the incipient superconducting transition.

Next we consider the bonding parameters of the DWS and their behavior across T_c . In general for $20 \text{ K} \leq T \leq 300 \text{ K}$, the DWS geometry exhibits little temperature dependence as the As1-Cr1(2) and Cr1-Cr1(2) bond lengths change by $\sim 0.3\%$ while the As2-Cr1(2) and Cr2-Cr2

bond lengths do not change within the sensitivity of our measurements (Fig. 2(a) and (b)). The relatively minor $\sim 0.4\%$ expansion seen in this temperature range along the c -axis is accounted for by the inter plaquette spacing while the thermal expansion along the a -axis affects the inter-DWS spacing (via As-K bond lengths). The significant metal-pnictide bond-length rigidity seen here is similar to that reported for FBS (Fig. 2(a))^{25,27,40}. This is likely due to the strong anti-bonding character of these bonds as determined in Ref. 7.

Below 20 K a shift in the DWS bonding behavior is observed. As shown in Fig. 2(b), the previously stoic Cr-Cr bond-lengths begin to exhibit temperature dependence. The Cr1(2)-Cr1(2) bonds dilate(contract) by 0.7% (0.9%) as the material is cooled from 13 to 0.5 K - a change larger than twice that from 300 to 20 K. A corresponding contraction (dilation) of 0.2% (0.24%) is seen in the As1(2)-Cr1(2) bonds. This describes an adjustment of the intra-CrAs plaquette bonding where the larger Cr2 triangle contracts and the Cr1 triangle dilates while the surrounding As matrix remains rigid (as evidenced by the changing As1(2)-Cr1(2) bond lengths) and the inter-DWS spacing remains unchanged (Fig. 2(a-b)). The previously discussed c -axis contraction causes a decrease in the inter-plaquette spacing due to the Cr sites' Wyckoff positions' fixed z components.

The cumulative effect is a decrease in the non-centrosymmetry of the DWS tubes, which can be quantified (as suggested in Ref 31) as $\Delta = \alpha - \beta$ (where α and β denote the As2-Cr2-As2 and As1-Cr1-As1 bond angles respectively Fig. 1(f)). Upon decreasing temperature α closes and β widens leading the parameter Δ to decrease from 3 at 13 K to 2.3 at 0.5 K (Fig 2(c)). This is somewhat unexpected in light of pressure effect studies that indicated a positive correlation between T_c and Δ ³¹. However, we argue that this decrease is a secondary effect due to competition between superconductivity and short-range magnetic order rather than a direct structural effect of superconductivity.

To probe for incipient magnetic order inelastic neutron scattering experiments were performed focusing on low momentum and energy transfers. Fig. 3(a) shows a neutron spectra intensity map of the dynamic structure factor $S(Q, E)$ collected at 10 K. A broad column of scattering from $0.75 \text{ \AA}^{-1} \leq Q \leq 1.20 \text{ \AA}^{-1}$ is clearly seen. The low Q and E values of this feature indicate that it is not likely due to phonons which exhibit a Q^2 in $S(Q, E)$ and have a calculated cutoff in $\text{K}_2\text{Cr}_3\text{As}_3$ of $\sim 4 \text{ meV}$ ^{18,41}. E integrated plots (Fig. 3(c)) for data collected at 1.5, 10, 100 and 200 K show a T -dependent peak-like feature at $\sim 1.2 \text{ \AA}^{-1}$ visible for $T < 200 \text{ K}$. Fig. 3 (d-f) show subtractions of the E -summed data from 10 K. For 100 K - 10 K (Fig. 3(e)), no appreciable change in intensity near $\sim 1.2 \text{ \AA}^{-1}$ is observed with the contribution to the difference curve coming only from the increased phonon background at 100K which exhibits the characteristic Q^2 dependence. On the other hand, 200 K - 10 K (panel (d)) exhibits a dip in the intensity at $Q \sim 1.2 \text{ \AA}^{-1}$ indicat-

ing that the column of scattering is either not present or has a reduced intensity by 200 K. Similarly, 10 K - 1.5 K (panel (b)) also reveals an intensity difference centered near 1.2 \AA^{-1} . The inelastic signal is suppressed not only at high temperatures but also below T_c - significantly this is consistent with both the results of local probes of the dynamic magnetism in $\text{K}_2\text{Cr}_3\text{As}_3$ (nuclear quadrupole resonance (NQR) and Knight shift (KS)) which have suggested short-range magnetic order^{12,42,43}. Furthermore, the column closely resembles similar measurements of incipient magnetic order reported for the FBS FeSe and LiFeAs^{12,42-45}.

The Q onset of the column $\sim 0.75 \text{ \AA}^{-1}$ (see Fig. 3(a)) is commensurate with a q vector $q_m = (00\frac{1}{2})$ which indexes the feature with hkl of $00\frac{1}{2}$ in the nuclear structure. Using representational analysis (as implemented in the ISODISTORT software Ref. 46) magnetic structures consistent with $q_m = (00\frac{1}{2})$ were explored one of which is shown in Fig. 3(g). This model is similar to the 'up-up-down-down' (UUDD) magnetic structure predicted in the DFT work of Wu *et. al.*⁶. The UUDD has Cr moments co-linear with the crystallographic c -axis and exhibits FM correlations within each plaquette, with FM coupling to the neighboring plaquette in one direction along the chain and AFM along the other (Fig. 3(g)).

To test the various magnetic structures consistent with q_m , Monte-Carlo simulations were performed using linear spin-wave theory (as implemented in SpinW Ref. 47) to model the observed inelastic scattering as spin-wave dispersions using the exchange interactions (J) predicted in Ref. 48. The simulated inelastic powder spectrum of the UUDD magnetic structure reproduces the general features of our experimental spectrum (Fig. 3(b)) (for more details see SM). The relatively small region of $S(Q, E)$ covered in our experiment does not allow for a unique determination of the incipient order or for a rigorous determination of the exchange interactions. In this model, the scattering originates of two acoustic spin-wave modes arising from reflections newly allowed by the UUDD structure: hkl of $00\frac{1}{2}$ and $10\frac{1}{2}$. We note that the general scale of the dispersions appear consistent with the predicted J values which put intra-DWS exchanges on the order of $\sim 10 \text{ meV}$ and inter-DWS J at $> 1 \text{ meV}$ (see SM). As the latter of these is increased the branches originating from hkl $00\frac{1}{2}$ and $10\frac{1}{2}$ become distinct and inconsistent with the measurement suggesting a weak but non-zero inter-DWS coupling.

The authors note that the observed suppression of spin-fluctuations below T_c provides a possible explanation for the change in the DWS geometry at T_c . In the metallic FBS magneto-elastic coupling is strong and spin-fluctuations are argued to drive the structural phase behavior affecting subtle bond changes and even structural transitions⁴⁹⁻⁵². We speculate that a similar scenario is possible in the metallic $\text{K}_2\text{Cr}_3\text{As}_3$ where changes to the Cr-Cr bonding below T_c may be driven by the reduction of magnetic fluctuations on the Cr sites. In the model shown in Fig 3(g), the reduction of short-range FM

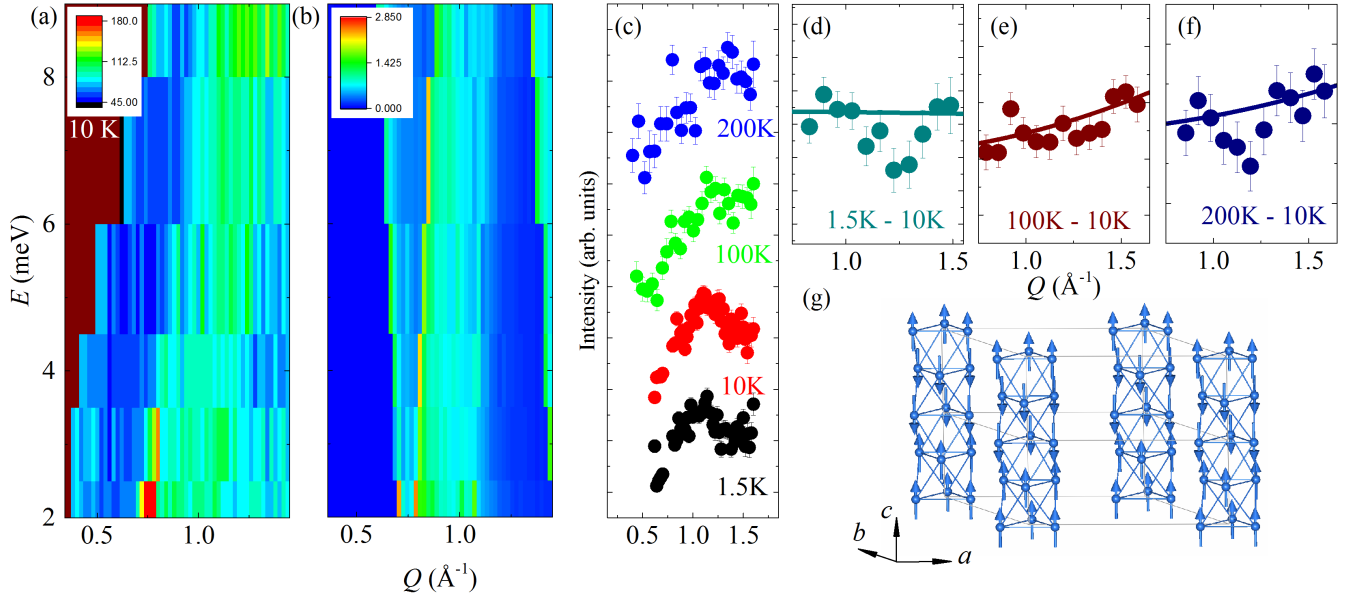


FIG. 3. Neutron spectra intensity map of the dynamic structure factor with the intensity normalized to the monitor (a). Simulated spin-wave dispersions of the Uudd magnetic structure with arbitrary intensity scale (b). Q dependence of the scattering intensity for E summed over 2-9 meV for all measured temperatures (c) each temperature is offset by an arbitrary y value for visual clarity. Difference curves for the 10 K summed intensity subtracted from the 1.5 K (d), 100 K (e) and 200 K (f) summed intensities. Lines are added to the plots as guides to the eye. Uudd magnetic structure consistent with $Q \sim 0.75 \text{ \AA}^{-1}$ (magnetic space group $Pc3c1$) (e).

correlations within each plaquette could relax the Cr-Cr bonds (Fig. 2(b)). Similarly the slight reduction of the c -axis near T_c could result from weakened AFM next nearest plaquette couplings. Irrespective of the magnetic model, predictions of a larger magnetic moment on the Cr2 site anticipate its stronger response to reduced spin-fluctuations in the presence of magneto-elastic coupling which is consistent with our results (Fig. 2(b))⁶. Generally, such an interpretation agrees remarkably well with recent Raman scattering experiments, which report the sudden softening and hardening of Cr modes at $T < 100$ K prospectively due to strong magneto-elastic coupling⁵³. Together with our results this suggests the possible importance of incipient magnetic order to the dynamics of this material and informs the need for further study of its short-range orders.

In conclusion, we report results of temperature dependent neutron powder diffraction and spectroscopy experiments. Diffraction data collected between 300 and 0.5 K reveal no signature of a structural phase transition or of the predicted long-range magnetic orders. However, careful inspection of the low temperature thermal expansion shows a subtle response of the c -axis to the onset of superconductivity. Analysis of the internal bonding of the DWS reveal a similar response to T_c where the CrAs plaquettes become less non-centrosymmetric due to a strong contraction of the Cr2-Cr2 bond length. Neutron spectroscopy experiments show the presence of a

column of scattering centered at a wave-vector $q_m = 00\frac{1}{2}$ which is suppressed below T_c and exhibits a Q dependence consistent with a magnetic origin. We propose that this inelastic signal indicates that $\text{K}_2\text{Cr}_3\text{As}_3$ is near a magnetic instability with a tendency to order possibly in an Uudd state. Spin-wave simulations of this structure replicate our observed inelastic signal and generally agree with predictions for the Cr-Cr magnetic interactions. Comparison of the Uudd magnetic structure with the observed bonding behavior at T_c is suggestive of competition between short-range magnetic order and superconductivity hinting at a situation similar to that of the FBS. Furthermore, the presence of incipient magnetic order with an AFM q_m lends support to spin-singlet models of superconductivity in these materials and suggests local fluctuations available for mediating electron pairing are AFM in nature.

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