Anomalous helimagnetic domain shrinkage due to the weakening of Dzyaloshinskii-Moriya interaction in CrAs

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CrAs is a well-known helimagnet with the double-helix structure originating from the competition between the Dzyaloshinskii-Moriya interaction (DMI) and antiferromagnetic exchange interaction J. By resonant soft X-ray scattering (RSXS), we observe the magnetic peak (0 0 qm) that emerges at the helical transition with T_S ≈ 265.5 K. Intriguingly, the helimagnetic domains significantly shrink on cooling below ~255 K, opposite to the conventional thermal effect. The weakening of DMI on cooling is found to play a critical role here. It causes the helical wave vector to vary, ordered spins to rotate, and extra helimagnetic domain boundaries to form at local defects, thus leading to the anomalous shrinkage of helimagnetic domains. Our results indicate that the size of magnetic helical domains can be controlled by tuning DMI in certain helimagnets.

In correlated materials, multiple magnetic interactions, including the superexchange, Dzyaloshinskii-Moriya interaction (DMI), Kondo coupling, Ruderman-Kittel-Kasuya-Yosida interaction, may co-exist, and they favor different ground states. The competition between these magnetic interactions leads to rich and novel phenomena such as the quantum criticality in Kondo lattice, spin liquid states in frustrated systems, and the emergence of magnetic skyrmions in helimagnets. Tuning the strength of these interactions would be a important way to engineer the magnetic quantum states and properties. Take a helimagnet system for example, its magnetic Hamiltonian can be generally written as:

\[ H = \sum_{i,j} \vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j) + J_{i,j} \vec{S}_i \cdot \vec{S}_j \quad (1) \]

in which \( \vec{D}_{ij} \) and \( J_{i,j} \) denote the anti-symmetric DMI and the symmetric exchange interactions between \( \vec{S}_i \) and \( \vec{S}_j \), respectively. By changing temperature, magnetic field, material thickness, or pressure, the system can be continuously tuned into helical, conical, Skyrme crystal or other quantum phases depending on the subtle balance of DMI, \( J \), Zeeman coupling, and thermal fluctuations. Especially, the nano-sized helimagnetic domains, a key ingredient for spintronics, can be delicately manipulated by external fields. For example, in-situ Lorentz microscopy of Fe_{0.5}Co_{0.5}Si film showed that magnetic field can effectively deform, rotate and enlarge the helimagnetic domains by applying \( H \) along different directions. Similar observation was recently reported in Te-doped Cu_2OSeO_3. Here, in the helimagnet CrAs, we observe an anomalous shrinkage of helimagnetic domains with decreasing temperature and find the decrease of DMI in CrAs on cooling as its main driving force. This is a quantum effect opposite to conventional thermal behavior and may be harnessed for domain engineering in spintronics.

The helical transition temperature of CrAs is \( T_S = 265 \text{ K} \) and its spin helix propagates along the c axis (Fig. 1(b)). The local space-inversion symmetry breaking at the Cr and As sites gives rise to DMI, which is essential in stabilizing the double-helix spin structure as revealed by group-theoretical approach. Compared with other helimagnets in the MnP-type structure, such as MnP and FeP, the DMI in CrAs is much more pronounced. In addition, recent studies show CrAs exhibits novel non-Fermi liquid behavior, unconventional superconductivity, and quantum criticality under certain conditions, and the helical magnetism is believed to be crucial on these fascinating properties. The strong DMI and rich quantum phases in CrAs make it an exciting playground to study the behavior of magnetic domains under the competition between DMI and \( J \).

In our experiment, we used soft X-ray absorption and resonant scattering to study the helical magnetism of CrAs. The magnetic resonant peak (0 0 qm) was observed at the chromium L-edge. Thanks to the high momentum resolution of resonant soft X-ray scattering (RSXS) technique, we could reveal the average helimagnetic domain...
size $\xi$ and its temperature-dependent evolution. Intriguingly, unlike conventional magnets whose magnetic domains always grow larger on cooling, the domain size of CrAs substantially decreases with lowering temperature below $\sim 255$ K. The average domain size in the ac plane shrinks by $\sim 44.14\%$ from 255 K to 20 K. We find that the temperature dependent domain shrinkage follows the weakening of DMI, whose competition with $J$ varies the helimagnetic wave vector. As the helical magnetic chains propagate across the crystal defects with decreasing DMI on cooling, extra helix domain boundaries form and the average domain size decreases, leading to the observed domain shrinkage opposite to the conventional thermal effect.

CrAs single crystals were grown by the Sn-flux method described in previous report[23]. The obtained shiny crystals have needle-like shape with a typical size of $6 \times 1 \times 0.5$ mm$^3$. The largest crystalline plane is $(0 0 1)$. RSXS and X-ray absorption (XAS) experiments on a CrAs single crystal were performed using a four-circle diffractometer at the Resonant Elastic and Inelastic X-ray Scattering (REIXS) beamline of Canadian Light Source (CLS). The REIXS beamline is equipped with Elliptical Polarized Undulators (EPU) and can provide both $\sigma$ and $\pi$ polarized incident photons. The momentum resolution of the RSXS instrument is better than $0.0005$ Å$^{-1}$ at 570 eV. For RSXS signal, a silicon photodiode was used, while for the XAS in total electron yield (TEY) mode and total fluorescence yield (TFY) mode were collected using a drain current and micro-channel plate (MCP) detector, respectively.

Figure 1(a) is the XAS of CrAs (red line) measured by TEY at the Cr $L$-edge. In order to elucidate the Cr valence state, the XAS of Cr$_2$O$_3$ and CrO$_2$ were plotted together as the fingerprint of Cr$^{3+}$ and Cr$^{4+}$ valence states[22], respectively. The bulk sensitive TFY spectrum of CrAs was simultaneously collected. Both the TEY and TFY spectra of CrAs are consistent with the typical Cr$^{3+}$ spectrum. These results show that the sample surface is clean and the valance state is Cr$^{3+}$ with the 3d$^3$ electronic configuration. The spin-only magnetic moment of Cr$^{3+}$ is 3.87 $\mu_B$, however, the observed value is 1.7 $\mu_B$[24]. The reduction of magnetic moment in CrAs should come from fluctuations and hybridization effect, similar to the case in MnP[25].

In our RSXS experiment, the scattering crystalline plane is ac and the momentum transfer direction is along (0 0 L) (Fig. 1(b)). In this configuration, the electric field of horizontally (vertically) polarized incident photons are perpendicular (parallel) to the b axis. In the helical state below $T_S$, the Cr$^{3+}$ spin moments lie in the ab easy plane, and the magnetic propagation wavevector is about $(0 0 0.356)$ at $T=4$ K[13]. From sample alignment, we determined the lattice constants are $a=5.412(9)$ Å, $b=3.348(1)$ Å, $c=6.007(9)$ Å at 20 K. Figure 1(c) presents the $L$ scans around the magnetic wavevector $k_{\parallel}=(0 0 q_m)$ with the resonant (E = 578.7 eV; $\pi$ polarization) and non-resonant (E = 570 eV, $\pi$ polarization) energies at $T=20$ K. Strong resonant peak appears around $(0 0 0.352)$, consistent with the previously reported helical propagation wavevector[24]. The blue dashed line in Fig. 1(c) is from neutron diffraction measurement on CrAs single crystal which is much broader due to its relatively low momentum resolution. A detailed comparison of neutron diffraction and RSXS experiments on CrAs can be found in the Supplemental Material.

To verify the magnetic nature of the $(0 0 q_m)$ peak, we measured its resonant profiles as a function of X-ray energy and wavevector $(0 0 L)$ at $T = 20$ K (Fig. 2). The incident X-ray is either vertically ($\sigma$, Fig. 2(a)) or horizontally ($\pi$, Fig. 2(b)) polarized. No distinction was made on the polarization of scattered photons, so the detected scattering intensities in our experiment are
$I_\pi = I_{\pi \sigma} + I_{\pi \sigma'}$ and $I_\sigma = I_{\sigma \sigma} + I_{\sigma \sigma'}$. The observed results show that $I_\pi$ is about 1.7 times stronger than $I_\sigma$. We further integrate the resonant intensity in Fig. 2(a) and (b) along the $L$ direction and get the $q$-integrated intensities $I_{\sigma}^{int}$ and $I_{\pi}^{int}$, as shown in Fig. 2(c). The lineshape profiles of $I_{\sigma}^{int}$ (black line) and $I_{\pi}^{int}$ (red line) are similar, except the latter is apparently stronger. The polarization dependence of resonant profiles is consistent with magnetic scattering from a helimagnet, as evidenced by the following theoretical analysis. The scattering intensity from a helimagnet can be expressed as $I_{mag} = |f_{mag}|^2$, and $|f_{mag}|$ is the resonant magnetic scattering length [28-29]:

$$f_{mag} = \left(\begin{array}{c} f_{\sigma \sigma'} \\ f_{\sigma \pi'} \\ f_{\pi \pi'} \end{array}\right) = -iF^1 \begin{pmatrix} 0 & M_a \cos \theta + M_c \sin \theta \\ M_c \sin \theta - M_a \cos \theta & -M_b \sin 2 \theta \end{pmatrix}$$

where $\sigma'$ and $\pi'$ denote the polarization of outgoing photons, $\theta$ is the angle between the incident X-ray and the sample surface, and $M_a$, $M_b$, $M_c$ are the spin moment along the three crystal axes. In our case, $M_a = M_b$, $M_c = 0$, so $|f_{\sigma \pi'}| = |f_{\pi \sigma'}|$. $I_\sigma = I_{\sigma \sigma} = I_{\sigma \sigma'}$. In this way, $I_\pi = I_{\pi \pi} + I_{\pi \sigma'} > I_\sigma$, so $I_\pi$ is always stronger than $I_\sigma$ within the Cr $L$-edge resonant energy range, this is consistent with the experiment observation shown in Fig. 2.

Detailed study on the temperature-dependent evolution of $(0 0 q_m)$ resonant peak was conducted by using the $\pi$-polarized incident photon with the resonant energy 578.7 eV. Both $L$ and $H$ scans were performed at the temperature range from 267.5 K to 20 K, as shown in Fig. 3(a) and 3(b). Along $L$ scans, $q_m$ continuously decreases on cooling, consistent with our neutron diffraction results shown in the Supplemental Material. The $L$ and $H$ scans take the Lorentzian and Gaussian lineshapes, respectively [Fig. 3(a) and 3(b)], indicating different domain size distribution along the $c$ and $a$ axes. This anisotropy may come from the unique propagating direction of the helimagnetic wavevector or the elongated needle-like crystal shape, both of which are along $c$ axis and could cause anisotropic grain and strain distribution.
inside the sample.

The temperature-dependent evolutions of peak intensity, propagation wavevector \( q_m \), and the average helimagnetic domain size \( \xi \) (\( \xi = 1/FWHM \), FWHM is for full-width-at-half-maximum) in \( L \) and \( H \) scans are presented in Fig. 3(c)-(e). In Fig. 3(c), the magnetic peak intensity rapidly saturates below \( T_S \), consistent with the first order transition character[13]. The change of \( q_m \) with decreasing temperature (Fig. 3(d)) indicates that the balance of competition between different magnetic interactions in CrAs varies with temperature. The average helimagnetic domain size \( \xi_c \) and \( \xi_a \) rapidly grow from \( T_S \) to 255 K (Fig. 3(e)), consistent with the typical critical behavior near a transition point[29]. However, below \( \sim 255 \) K both \( \xi_c \) and \( \xi_a \) abnormally decrease on cooling (Fig. 3(e)). The broadening of the magnetic peak also leads to a slight decreasing of peak intensity along \( H \) (Fig. 3(c)). Usually, the average helimagnetic domain size of a magnetic order should monotonically increase below \( T_S \) because thermal fluctuations are weakened and spins become more correlated on cooling. The anomalous \( \xi \) versus \( T \) in CrAs indicates the average helimagnetic domain size actually shrinks with lowering temperature. Cooling and warming sequences (see Supplemental Material) show little thermal history effect in the temperature-dependent evolution of \( \xi \) and \( q_m \).

The anomalous shrinkage of magnetic domains on cooling can be interpreted by the weakening of DMI in CrAs. In ref. 13, the authors gave a detailed description on the magnetic interactions in CrAs. Its magnetic Hamiltonian was represented by Eq. 1, in which \( D_{i,j} \) and \( J_{i,j} \) are the DMI and antiferromagnetic interactions between the nearest neighbors, respectively. The nearest-neighboring spins in a single unit cell are illustrated by the red dashed lines in Fig. 1(b). \( q_m \) can be expressed as[13]:

\[
q_m = \frac{\beta_{12} + \beta_{23}}{\pi}
\]

where \( \beta_{12} \) is the angle between \( \vec{S}_1 \) and \( \vec{S}_2 \), \( \beta_{23} \) is the angle between \( \vec{S}_2 \) and \( \vec{S}_3 \). In the temperature range of our study, \( \beta_{23} \) barely changes[13]. Therefore, the decrease of \( q_m \) on cooling is mainly attributed to the variation of \( \beta_{12} \), which is determined by:

\[
\beta_{12} = \tan^{-1}(D_{12}/J_{12})
\]

in which \( D_{12} \) is the \( \vec{D}_{12} \) component along the \( c \) axis. There are antiferromagnetic interactions between all nearest spins, in contrast, DMI exists between \( \vec{S}_1 \) and \( \vec{S}_2 \) but is absent between \( \vec{S}_2 \) and \( \vec{S}_3 \)[13]. Moreover, the DMI in CrAs is exceptionally larger than the antiferromagnetic interaction (\( |D|>|J| \)) [14]. Therefore, the induced change of \( \beta_{12} \) and the decreasing of \( q_m \) should be dominated by the variation of \( D_{12} \):

\[
\Delta(q_m) \propto \Delta(D_{12})
\]

According to this equation, the 6.70\% decrease of propagation wavevector, from \( q_m=0.3773(5) \) at 255 K to \( q_m=0.3520(6) \) at 20 K, indicates that \( D_{12} \) becomes weaker. Since \( D_1 \) favors non-collinear spin alignment and \( J_{12} \) favors antiparallel spin alignment in CrAs[13], \( \vec{S}_1 \) and \( \vec{S}_2 \) tends to be more antiparallel[13], as illustrated by \( \beta_{12} \) in Fig. 4. This again evidences the weakening of DMI with decreasing temperature. As DMI is the dominant force determining the spin rotation along the helix chain, its weakening will make the helimagnetic domains easier to break up at the defect sites. As \( q_m \) varies with temperature, the neighboring spins continuously modulate their relative spin angles on cooling, which would generate additional domain boundaries at defect sites given the weakening DMI, in other words, the helimagnetic domains shrink. A straightforward cartoon illustration for the DMI controlled spin angle \( \beta_{12} \) and the accompanied domain shrinkage is presented in Fig. 4.

The helimagnetic domain shrinkage is anisotropic and mainly takes place along the \( c \) direction. As shown in Fig. 3(e), from 255 K to 20 K the percentage drop of \( \xi_c \) and \( \xi_a \) are 38.44 \% and 9.26 \%, respectively. Here we define the spatial anisotropic ratio of domain shrinkage as \( \gamma_{ca} = \Delta \xi_c/\Delta \xi_a \). This is consistent with the fact that the helimagnetic order is propagating along the \( c \) direction. Meanwhile, it is intriguing to note that the DMI of CrAs is \( \vec{D}_{12} \approx D_0(-0.17, -0.5, 0.85)[13] \), so the ratio of DMI components along \( c \) and \( a \) is \( \kappa_{ca} = |D_{12}/D_0| = 5.7 \). The similar size of \( \gamma_{ca} \) and \( \kappa_{ca} \) implies possible role played by DMI in the anisotropy of domain shrinkage, as certain interactions exist in \( a \) and \( b \) directions as well.

By contrast, in our previous RSXS investigation on
MnP, a helimagnet similar to CrAs in lattice and magnetic structures but its propagation wavevector increases on cooling |3|, the domain shrinkage behavior was not observed |25|. This implies that the decrease of $q_m$ or DMI on cooling is the key to the formation of new domain boundaries at defect sites inside the sample. It should be noted that in most 3$d$-transition metal pnictides the strength of DMI is much smaller than $J$, however, CrAs is an exception in which $|D|>|J|$ |14|. The strong DMI of CrAs even drives the spin reorientation transition and decrease of magnetic wavevector under pressure |13|. Therefore, we conclude that the pronounced DMI strength combined with its decrease on cooling are essential ingredients for the anomalous helimagnetic domain shrinkage behavior in CrAs. Broadening of magnetic peak at low temperature was also observed in Ca$_3$Co$_2$O$_6$ with ferromagnetic chains, while it is attributed to the development of a short range order |20|, which is distinct from the single-component magnetic peak in CrAs and does not involve DMI.

In summary, we find the Cr$^{3+}$ valence state in CrAs and our RSXS experiment reveals its helimagnetic domains shrink on cooling below $\sim 255$ K. The domain shrinkage has similar temperature-dependent evolution with that of DMI, indicating DMI is the main driving force in this anomalous behavior. Our results reveal a quantum effect that is opposite to conventional thermal effect, and suggest that DMI may be tuned to manipulate the domain boundaries in helimagnets which may have application in future spintronics.

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Supplemental material for

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1. Sample characterization

We used Physical Properties Measurement System (PPMS) to characterize the electronic resistivity of the experimental sample from 300 K to 2 K, as shown in Fig. S1. The sample’s resistivity shows a transition into the helical magnetic phase at 263 K, in consistence with previous reports. The inset panel shows the CrAs crystal with needle-like shape.

![CrAs single crystal](image)

Figure S1: Resistivity of CrAs single crystal. The helical transition appears at $T_S=263$ K.

2. Comparison of the results from resonance soft X-ray scattering and neutron diffraction

We have performed both RSXS and neutron diffraction (ND) on CrAs single crystal for a comparative study. The RSXS experiment was carried out at the REIXS beamline of Canadian Light Source. Single crystal ND was measured at the SPINS cold triple-axis spectrometer of the NIST Center for Neutron Research. The momentum transfer $q$ is along the (0 0 $L$) direction in both experiments. The measured (0 0 $q_m$) magnetic peak at various temperatures by RSXS (E=578.7 eV, $\pi$ polarization) and ND are shown in Fig. S2(a) and (b), respectively. It is obvious that the peak width in RSXS data is much narrower, illustrating the instrumental resolution of RSXS is higher than that of ND. Actually, the RSXS’s instrumental resolution in our experiment is less than 0.0005 Å$^{-1}$ at 570 eV, much smaller than the resonance peak width of CrAs. This unique ability of RSXS directly gives us intrinsic magnetic peak
width or correlation length.

The magnetic peak intensity, propagation wavevector, and FWHM at various temperatures are shown in Fig. S2(c–e). It can be seen that RSXS and ND agree with each other at the temperature dependence of peak intensity and propagation wavevector. The FWHM of ND data are 7 times broader than that of RSXS data due to the relatively poor momentum resolution of ND.

Figure S2: Temperature dependence of the magnetic peak in CrAs single crystals probed by (a) RSXS and (b) neutron diffraction. The neutron diffraction peaks are much broader than the ones from RSXS. Comparison of the (c) peak intensity, (d) propagation wavevector, and (e) FWHM of RSXS (red dots) and neutron diffraction (black dots) as a function of temperature.

3. **Evolution of the (0 0 q_m) resonant peak on the cooling and warm up processes**

Detailed study on the temperature evolution of the (0 0 q_m) resonant peak was conducted by using π polarized incident photon with the energy $E = 578.7$ eV. The sample was first cooled down from above $T_S$ to 20 K (step 1), and then warmed up back to above $T_S$ (step 2). The raw data of $L$ scans at several temperatures are shown in Fig. S3(a,b). The solid lines are fittings by the Lorentzian function. The peak intensity and correlation length are shown in Fig. S3(c,d). There is no obvious difference between the $L$ scans in the cooling and warm up processes, suggesting the temperature evolution of magnetic domains has little dependence on thermal history.
Figure S3: (a) Temperature evolution of the (0 0 \textit{q_m}) resonant peak along the \textit{L} direction with incident photon \( E = 578.7 \) eV, \( \pi \)-polarization. The sample was first (a) cooled down from above \( T_S \) to 20 K (step 1), and then (b) warmed up back to 267.5 K (step 2). The solid lines are Lorentzian fittings. Temperature dependence of (c) resonant peak intensity and (d) correlation length \( \xi_c \) in the cooling (blue circles) and warm up (red dots) processes.