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Phys. Rev. B **93**, 060503 — Published 1 February 2016

DOI: [10.1103/PhysRevB.93.060503](https://doi.org/10.1103/PhysRevB.93.060503)

Structural and magnetic phase diagram of CrAs and its relationship with pressure-induced superconductivity

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We use neutron diffraction to study the structure and magnetic phase diagram of the newly discovered pressure-induced superconductor CrAs. Unlike most magnetic unconventional superconductors where the magnetic moment direction barely changes upon doping, here we show that CrAs exhibits a spin reorientation from the *ab* plane to the *ac* plane, along with an abrupt drop of the magnetic propagation vector at a critical pressure ($P_c \approx 0.6$ GPa). This magnetic phase transition accompanied by a lattice anomaly coincides with the emergence of bulk superconductivity. With further increasing pressure, the magnetic order completely disappears near the optimal T_c regime ($P \approx 0.94$ GPa). Moreover, the Cr magnetic moments tend to be aligned antiparallel between nearest neighbors with increasing pressure toward the optimal superconductivity regime. Our findings suggest that the non-collinear helimagnetic order is strongly coupled to structural and electronic degrees of freedom, and that the antiferromagnetic correlations between nearest neighbors might be essential for superconductivity.

Most unconventional superconductors, including cuprates and iron-based superconductors, are derived from chemical doping or application of pressure on their collinearly magnetic-ordered parent compounds [1–5]. The recently discovered pressure-induced superconductor CrAs, as a rare example of a non-collinear helimagnetic superconductor, has therefore generated great interest in understanding microscopic magnetic properties and their interplay with superconductivity [6–8]. Previous measurements have shown that CrAs exhibits a first order non-collinear helimagnetic phase transition accompanied by a magnetostriction below $T_N \approx 270$ K [9–13]. The resistivity of CrAs also displays a clear anomaly around the Néel temperature [6, 7, 14]. This anomaly is suppressed progressively under pressure and fades away at $P > 0.6$ GPa, before bulk superconductivity appears [6, 7, 15]. The maximum $T_c \approx 2$ K is attained at $P \approx 1$ GPa, above which T_c decreases with increasing pressure [6, 7]. It has also been revealed that the nuclear spin-lattice relaxation rate in CrAs shows substantial magnetic fluctuations, but does not display a coherence peak in the superconducting state, indicating an unconventional pairing mechanism [15]. Moreover, neutron diffraction measurements suggested that pressure does not change the magnetic structure but partially suppresses the magnetic ordering moment at $P \leq 0.65$ GPa (ref. 16). However, there was significant pressure inhomogeneity in the cell with a fluorocarbon-based fluid pressure medium in ref. 16, as two sets of Bragg peaks were visible [17]. Therefore, the precise crystal and magnetic structure under pressure remains unsettled [17]. This elucidation is important to establish whether and what kind of magnetism is directly associated with superconductivity in this system.

We used neutron diffraction to study the structural and magnetic ordering properties of CrAs. A high quality polycrys-

talline sample was synthesized as reported in ref. 13. Our measurements were carried out on the BT-1 powder diffractometer, SPINS cold triple-axis spectrometer, and BT-7 thermal triple axis spectrometer at the NIST Center for Neutron Research [18].

Fig. 1c illustrates the diffraction pattern at 4 K at ambient pressure, which can be described by a non-collinear double helimagnetic structure (Fig. 1a). Similar to earlier work [10, 16], the Cr magnetic moment $[1.724(9)\mu_B]$ lies in the *ab* plane, and the helical propagation vector is $\vec{k} = (0, 0, 0.35643)$. To determine the evolution of the magnetic structure under pressure, we carried out more measurements in an aluminium alloy ($P < 0.65$ GPa) or steel ($P > 0.65$ GPa) pressure cell. Helium was used as the pressure medium to minimize pressure inhomogeneity [17]. Fig. 1d shows the diffraction pattern at $P = 0.4$ GPa and $T = 4$ K. Magnetic refinements confirm that the magnetic structure is similar to that at ambient pressure, except for the slightly reduced propagation vector $(0, 0, 0.3171)$ and moment $[1.71(2)\mu_B]$. The change of the magnetic propagation vector was not found in previous work at a similar pressure [16, 17]. Most notably, the diffraction pattern at $P = 0.6$ GPa (Fig. 1e) shows substantial changes of the magnetic reflections compared to those at ambient and low pressures, indicative of a magnetic phase transition. Our refinement analysis reveals that these changes are due to a spin reorientation from the *ab* plane to the *ac* plane together with a rapid decrease of magnetic propagation vector to $\vec{k} = (0, 0, 0.2080)$, as shown in Fig. 1b. It should be noted that this spin reorientation does not conflict with earlier NMR measurements [15], because the weak and broad NMR spectra observed at $P > 0.53$ GPa cannot distinguish the spin directions revealed by current neutron measurements. In addition, the nuclear peaks can be described by an orthorhombic

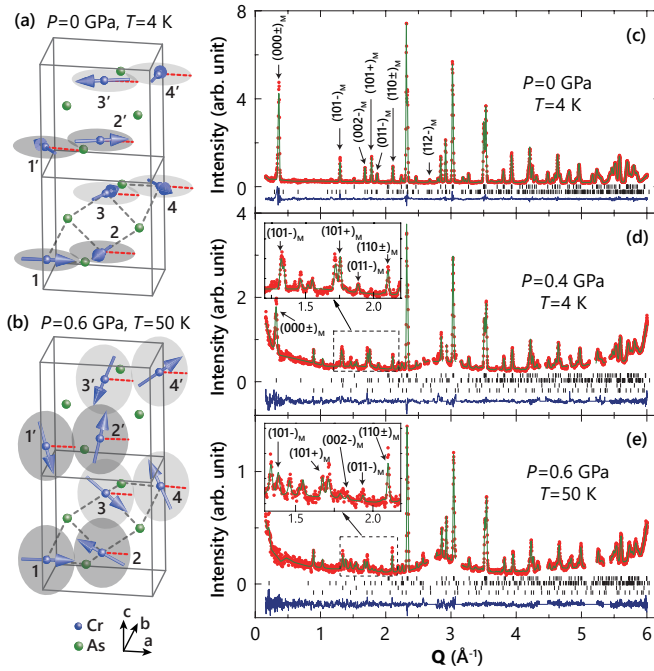


FIG. 1. Pressure dependence of the magnetic structure for CrAs. (a), (b) Magnetic structures at $P = 0, 0.6$ GPa, respectively. The red dashed lines indicate the direction of moment 1. (c) Observed (red) and calculated (green) diffraction intensities at $P = 0$ GPa and 4 K. (d) The diffraction pattern at $P = 0.4$ GPa and $T = 4$ K. The four refined phases are crystal and magnetic structures of CrAs, the second and third order neutron reflections from the aluminium pressure cell. The missing data correspond to the strong first order neutron reflections from the aluminium pressure cell. (e), The diffraction pattern at $P = 0.6$ GPa and $T = 50$ K.

$Pnma$ space group. The refined structural and magnetic parameters at representative temperature and pressure are given in Table I.

Figure 2 summarizes the structural and magnetic phase transitions under various pressures. At ambient pressure, the $(0, 0, 0)\pm$ magnetic peak abruptly disappears on warming to $T_N = 272$ K (Figs. 2a and 2k). Similar behavior is also observed at $P = 0.4$ GPa (Figs. 2c and 2l). At the critical pressure $P_c = 0.6$ GPa, the magnetic peak shows a spin reorientation behavior from the ab plane to the ac plane below $T_r = 88$ K (Figs. 2e and 2m). With further increasing pressure to $P = 0.72, 0.82$ GPa, the magnetic moment stays in the ac plane, while its magnitude is further reduced. Accompanied by the magnetic phase transitions, structural phase transitions are also observed (Figs. 2b, 2d, 2f, 2h, 2j, and 2k-2o), even though the crystal symmetry remains unchanged below and above the Néel temperature. The temperature-dependent profile of nuclear peaks shows a sudden shift near the Néel temperature, indicative of discontinuous changes of lattice parameters (Figs. 2b, 2d, 2f, 2h, 2j and 4a-4c).

Fig. 3a summarizes the pressure and temperature dependence of the propagation vector. Obviously, the propagation vector decreases gradually with decreasing temperature

at $P = 0$ and 0.4 GPa, when the magnetic moment is in the ab plane, which is similar to previous results at ambient pressure [10]. Conversely, the propagation vector actually increases slightly with decreasing temperature at $P = 0.72, 0.82$ GPa, when the magnetic moment has rotated to the ac plane. At $P_c \approx 0.6$ GPa, the propagation vector decreases drastically on cooling through $T_r = 88$ K, owing to the spin reorientation. The dramatically pressure- and temperature-dependent magnetic propagation vector observed here is different from the weakly pressure- and temperature-dependent spin density wave vector of metallic chromium [19, 20]. Moreover, the nearest neighbour Cr-Cr distances ($d = 2.856, 3.090,$ and 3.588 Å; $P = 0$ GPa, $T = 5$ K) in CrAs are larger than that (~ 2.498 Å) of chromium. These results together with the fact that the magnetic moment of CrAs is much larger than in metallic chromium ($\sim 0.6\mu_B$, ref. 19) suggest that Cr moments are more localized in CrAs.

To summarize the data in Figs. 1, 2 and 3a, we plot in Fig. 3b the structural and magnetic phase diagram of CrAs under pressure along with the superconducting transition temperatures determined from resistivity measurements [6, 7, 15]. Both the magnetic and structural phase transition temperature and the magnetic moment are gradually suppressed by pressure and eventually completely disappear at $P \approx 0.94$ GPa, where optimal T_c is realized (Figs. 3b and 3c). In contrast to previous resistivity measurements that suggest that the magnetic order is completely suppressed above $P > 0.6$ GPa [6, 7, 13], our neutron data show that the magnetic order and structural distortion persist at $P = 0.72, 0.82,$ and 0.88 GPa, where the resistivity anomaly disappears (Fig. 3b). As the pressure dependence of the propagation vector shows a sudden drop at $P_c \approx 0.6$ GPa (Figs. 3a and 3b), which is accompanied by the spin reorientation, the diminishing resistivity anomaly is very likely due to the spin reorientation transition. Interestingly, an anomaly on the Néel temperature vs. pressure curve is also observed at $P = 0.72$ GPa (Fig. 3b), probably due to the competition between the high propagation vector phase and the low propagation vector phase near the spin reorientation transition. More importantly, as shown in Fig. 3b, the contour propagation vector map and the superconducting transition temperature plot reveal that the emergence of superconductivity is directly associated with the spin reorientation and the subsequent decrease of the propagation vector. The superconducting volume fraction as a function of pressure further proves that the emergence of bulk superconductivity coincides with the drop of the propagation vector (Fig. 3c). These results indicate strong interplay between magnetism and superconductivity in this system. We note that a recent μ SR measurements also revealed the competition between the superconducting and the magnetic phase fractions in the similar pressure region [21].

Figure 4 illustrates the pressure effect of the lattice constants, Cr-Cr distances, and angles between Cr moments at various temperatures obtained from our refinement analysis. At ambient pressure, a large magnetostriction ($\Delta b/b=3.45\%$, $\Delta a/a=-0.29\%$, $\Delta c/c=-0.84\%$, $\Delta v/v=2.28\%$, $P = 0$ GPa) is

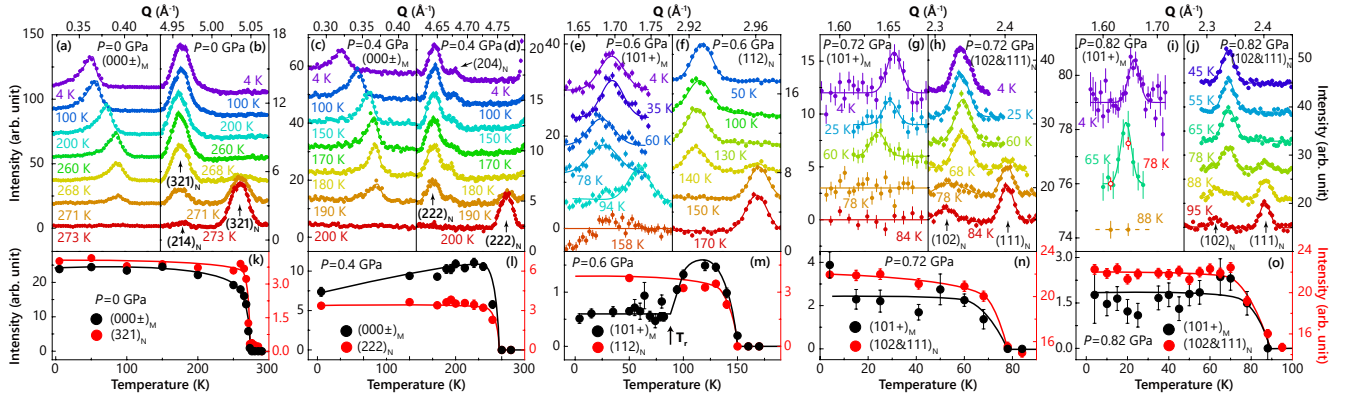


FIG. 2. Structural and magnetic phase transition temperatures at representative pressure for CrAs. All measurements were performed on warming after initially cooling to $T = 5$ K. (a)-(j) Temperature-dependent diffraction profile at various pressures. The subscript letters (M, N) denote magnetic and nuclear peaks, respectively. (k)-(o) Temperature dependence of the peak intensity of the data obtained in (a)-(j). We note that in (l), the decrease of the $(000\pm)_M$ peak intensity at low temperature is due to the decrease of the phase angle β_{12} on cooling, as shown in Fig. 4g. The error bars indicate one standard deviation.

TABLE I. Refined magnetic and structural parameters of CrAs under ambient and applied pressure. Space group: $Pnma$.

| $P(\text{GPa})$ | $T(\text{K})$ | $a(\text{\AA})$ | $b(\text{\AA})$ | $c(\text{\AA})$ | $m(\mu_B)$ | k -vector | $Rp(\%)$ | $wRp(\%)$ | χ^2 |
|-----------------|---------------|-----------------|-----------------|-----------------|------------|-------------|----------|-----------|----------|
| 0 | 4 | 5.60499(5) | 3.58827(3) | 6.13519(5) | 1.724(9) | 0.35643(7) | 4.82 | 5.87 | 1.55 |
| 0.4 | 4 | 5.5882(1) | 3.57937(7) | 6.1253(1) | 1.71(2) | 0.3171(2) | 4.73 | 5.95 | 2.00 |
| 0.6 | 50 | 5.5700(1) | 3.57003(9) | 6.1176(1) | 1.41(4) | 0.2080(4) | 5.86 | 7.05 | 1.10 |
| 0.72 | 4 | 5.556(5) | 3.564(1) | 6.102(2) | 1.25(10) | 0.1752(8) | 2.27 | 2.98 | 2.69 |
| 0.82 | 4 | 5.546(3) | 3.550(1) | 6.091(2) | 1.24(3) | 0.1706(8) | 5.63 | 7.74 | 2.44 |
| 0.88 | 4 | 5.541(2) | 3.546(2) | 6.074(8) | 1.0(2) | 0.144(6) | 7.28 | 9.85 | 3.73 |
| 0.94 | 1.5 | 5.6316(6) | 3.3585(4) | 6.2029(6) | 0 | - | 2.89 | 3.60 | 3.70 |

observed below the Néel temperature (Figs. 4a-4c). The increased volume of the unit cell below T_N naturally suggests that the magnetic order could be suppressed by reducing magnetostriction under pressure. However, the magnetostriction ($\Delta b/b=5.69\%$, $\Delta a/a=-0.88\%$, $\Delta c/c=-1.36\%$, $\Delta v/v=3.33\%$, $P = 0.6$ GPa) actually increases with increasing pressure. On the other hand, pressure significantly reduces the nearest neighbor Cr-Cr lengths (Figs. 4e and 4f), which could make the d electrons of Cr more itinerant, and therefore reduce the magnetic moment. More interestingly, the pressure dependence of the lattice parameters in the magnetically order state displays a clear anomaly at the critical pressure $P_c = 0.6$ GPa (Fig. 4d), which corresponds to the spin reorientation transition and the emergence of bulk superconductivity (Figs. 3b and 3c). These observations suggest a strong coupling between electronic, magnetic and lattice degrees of freedom. We also notice that the angle β_{12} between Cr moments S_1 and S_2 decreases drastically from $\sim -100^\circ$ (almost perpendicular) to $\sim -160^\circ$ (almost antiparallel) with increasing pressure $P > 0.6$ GPa (Fig. 4g). The angle β_{23} between S_2 and S_3 is close to 180° and barely changes with pressure (Fig. 4h). These results indicate that the moments between nearest neighbors tend to be antiferromagnetically aligned in the bulk superconductivity regime. If superconductivity is indeed mediated by fluctuations of the magnetic order in this system,

these results may suggest that antiferromagnetic fluctuations are crucial for superconductivity.

It is interesting to compare the electronic phase diagram of CrAs with that of other magnetic unconventional superconductors [1–3, 5, 22]. Unlike cuprates and iron based superconductors where chemical doping or application of pressure only reduces the magnitude of the magnetic moment while leaving the moment direction essentially unchanged [1, 2], pressure induces a spin reorientation transition in CrAs. The highly tunable non-collinear magnetic structure under pressure and the large magnetostriction observed in CrAs are likely due to the frustrated magnetic exchange interactions, which resembles the behavior of multiferroic materials with non-collinear magnetic structures [23]. Indeed, the decrease of the magnetic propagation vector can be qualitatively understood by considering a minimum magnetic exchange model and the Dzyaloshinskii-Moriya (DM) interactions [29, 30]. As shown in Figs. 1a and 1b, the interaction between spin \hat{S}_i and \hat{S}_j can be generally written as:

$$\hat{H}_{ij} = \vec{D}_{ij} \cdot (\hat{S}_i \times \hat{S}_j) + J_{ij} \hat{S}_i \cdot \hat{S}_j, \quad (1)$$

where \vec{D} and J are the DM interaction unit vector and nearest-neighbor exchange coupling, respectively. \vec{D}_{ij} is proportional to $(\vec{R}_{As_{ij1}} + \vec{R}_{As_{ij2}} - \vec{R}_{Cr_i} - \vec{R}_{Cr_j}) \times (\vec{R}_{Cr_i} - \vec{R}_{Cr_j})$, where $\vec{R}_{As_{ija}}$ are coordinates of the As atoms that link \hat{S}_i and \hat{S}_j spins [31].

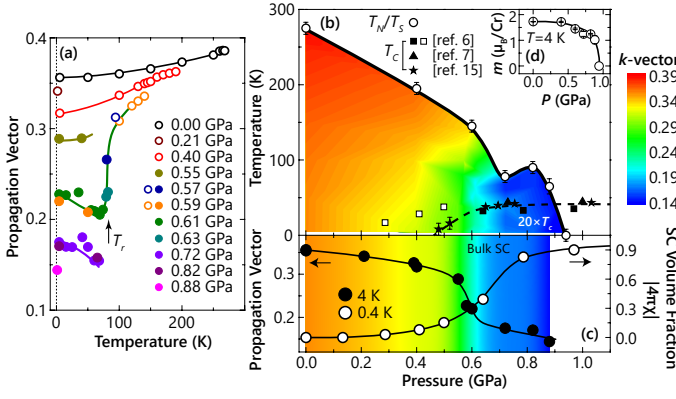


FIG. 3. Structural and magnetic phase diagram of CrAs. (a) Temperature and pressure dependence of the magnetic propagation vector. The open and filled circles indicate the magnetic moment in the ab and ac plane, respectively. (b) Structural and magnetic phase diagram of CrAs. The contour propagation vector map is plotted from the data in Fig. 3a in the temperature-pressure space. The superconducting transition temperatures are adapted from refs. 6, 7, and 15. (c) The pressure dependence of the propagation vector and the superconducting volume fraction determined by susceptibility measurements adapted from ref. 6. Different from refs. 7 and 15, indication of superconductivity was also observed at $0.29 \leq P \leq 0.5$ GPa in ref. 6 (open squares). However, in this pressure range, the superconductivity is filamentary rather than a bulk phenomenon because the superconducting volume fraction is extremely low ($\leq 15\%$) and the resistivity exhibits multiple superconducting transitions [6]. The superconducting volume fraction increases significantly above 0.6 GPa, when the spin-reoriented low-vector phase is fully developed. The same color code as in (b) is used, which indicates the amplitude of propagation vector. (d) The pressure dependence of the magnetic moment at 4 K.

Then we obtain $\vec{D}_{12} = \vec{D} \sim D_0(-0.17, -0.5, 0.85)$, $\vec{D}_{23} = 0$. By symmetry, we have $H_{12} = H_{34}$. Therefore, the minimum model to describe one helix chain along the c axis is given by

$$\hat{H} = \sum_i \vec{D} \cdot (\hat{S}_{i,1} \times \hat{S}_{i,2} + \hat{S}_{i,3} \times \hat{S}_{i,4}) + J_1(\hat{S}_{i,1} \cdot \hat{S}_{i,2} + \hat{S}_{i,3} \cdot \hat{S}_{i,4}) + J_1'(\hat{S}_{i,2} \cdot \hat{S}_{i,3} + \hat{S}_{i,1} \cdot \hat{S}_{i+1,4}). \quad (2)$$

With $J_1' > 0$, it accounts for the antiferromagnetic spin orientation between S_2 and S_3 . The angle β_{12} is given by $\tan(\beta_{12}) = \vec{D} \cdot \vec{n} / J_1$, where \vec{n} defines the helix spin rotation plane. The propagation vector $\vec{k} = (0, 0, \frac{2(\beta_{12} + \beta_{23})}{2\pi})$. As the component of \vec{D} along the c axis is larger than that along the b axis, the propagation vector decreases if the rotation plane changes from the ab plane [$\vec{n} = (0, 0, 1)$] to the ac plane [$\vec{n} = (0, 1, 0)$], since β_{23} is close to 180° in both phases.

The direct connection between the emergence of superconductivity and the spin reorientation has been observed in a ferromagnetic superconductor URhGe near a quantum critical point induced by magnetic field [24, 25], but has not been observed in other magnetic superconductors without a net macroscopic magnetic moment. Interestingly, the normal state resistivity of CrAs under pressure follows the power-law relationship, indicating the presence of a magnetic quantum

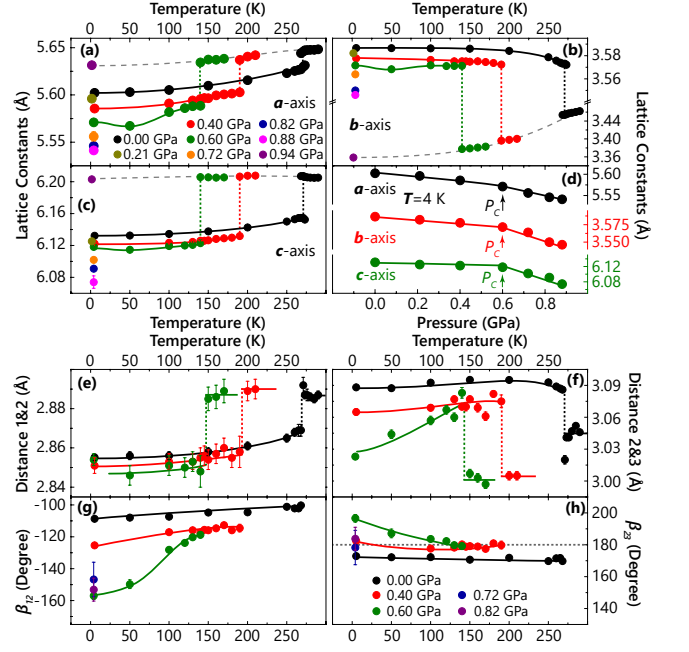


FIG. 4. Temperature and pressure dependence of lattice constants, Cr-Cr distances, and angles between Cr moments. (a)-(c) Lattice parameter as a function of temperature and pressure. When the magnetic order is fully suppressed at 0.94 GPa and 1.5 K, the lattice parameters are exactly in the extrapolation of curve obtained by considering the lattice parameters above T_N for $P = 0, 0.4$ and 0.6 GPa. (d) Pressure dependence of lattice parameter in the magnetically ordered state. (e) Distance between S_1 and S_2 (nearest-neighbor). (f) Distance between S_2 and S_3 (nearest-neighbor). (g) Angle (β_{12}) between spin S_1 and S_2 . (h) Angle (β_{23}) between spin S_2 and S_3 . By symmetry, we have $\beta_{12} = \beta_{34}$, $\beta_{23} = \beta_{41}$ (Figs. 1a and 1b).

critical point [6]. However, in contrast to URhGe, the spin reorientation in CrAs is also accompanied with an abrupt reduction of the magnetic propagation vector. Theoretical studies have shown that the spin fluctuations at a relatively large wavevector tend to lead to a singlet pairing while that at small wavevector close to $q = 0$ would favor a triplet pairing [1–5, 22, 26, 27]. If these theories apply in CrAs, it would imply that the pairing state in CrAs could be wavevector/pressure dependent. It is of great theoretical importance if the pairing symmetry could be tuned in a controlled manner in a helimagnetic superconductor [8]. Very recently, pressure induced superconductivity was also observed in a similar double helimagnet MnP (ref. 28). It would be interesting to see if the helical magnetic structure of MnP evolves in a similar way as that of CrAs at proximity of the superconducting dome.

In summary, we have determined the structural and magnetic phase diagram of CrAs under pressure. We show that CrAs exhibits a spin reorientation together with a rapid decrease of the magnetic propagation vector above the critical pressure ($P_c \approx 0.6$ GPa), where bulk superconductivity begins to emerge. Moreover, the nearest neighbor spins tend to be aligned antiparallel near the optimal superconductivity regime, which suggests that antiferromagnetic correlations

between nearest neighbors may be essential for superconductivity. The highly tunable magnetic moment direction and propagation vector observed in CrAs open up new avenues of research into the interplay between non-collinear helimagnetism and unconventional superconductivity.

This work is supported by the National Natural Science Foundation of China (No. 91421106 and No. 11374059), the the Ministry of Science and Technology of China (973 project: 2015CB921302), and the Shanghai Pujiang Scholar Program (No. 13PJ1401100). H.C. received support from the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy. Y.S., Q.W. and Y.H. contributed equally to this work.

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