Itinerant G-type antiferromagnetic order in SrCr$_2$As$_2$

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Neutron diffraction and magnetic susceptibility studies of a polycrystalline SrCr$_2$As$_2$ sample reveal that this compound is an itinerant G-type antiferromagnet below the Néel temperature $T_N = 590(5)$ K with the Cr magnetic moments aligned along the tetragonal c axis. The system remains tetragonal to the lowest measured temperature ($\sim 12$ K). The lattice parameter ratio $c/a$ and the magnetic moment saturate at about the same temperature below $\sim 200$ K, indicating a possible magnetoelastic coupling. The ordered moment, $\mu = 1.9(1)$ $\mu_B$/Cr, measured at $T = 12$ K, is significantly reduced compared to its localized value ($4 \mu_B$/Cr) due to the itinerant character brought about by the hybridization between the Cr 3$d$ and As 4$p$ orbitals.

I. INTRODUCTION

Extensive research has been devoted in recent years to iron-based pnictides and chalcogenides due to their intriguing correlated lattice, electronic, magnetic and superconducting properties [1,3]. In particular, comprehensive studies have been conducted on the doped and undoped body-centered tetragonal parent compounds $A$Fe$_2$As$_2$ ($A = $ Ca, Sr, Ba, Eu) with the ThCr$_2$Si$_2$-type structure (122-type compounds). This in turn prompted the search for novel physical properties in other transition-metal based 122-type compounds, such as with Mn/Fe in place of Fe [10–16], and moreover to CaMn$_2$As$_2$ and SrMn$_2$As$_2$ with the layered trigonal CaAl$_2$Si$_2$-type structure [17,18]. Experimental and theoretical work on BaCr$_2$As$_2$ with the ThCr$_2$Si$_2$-type structure [19,21] revealed metallic character, and an itinerant spin-density-wave ground state [21]. The theory also indicated stronger Cr–As covalency than occurs in the Fe–As compounds. BaCr$_2$As$_2$ undergoes G-type antiferromagnetic (AFM) ordering below a transition temperature $T_N = 580(10)$ K with moments aligned along the c axis [22]. ARPES measurements indicate reduction in electron correlation effects involving the nominally 3$d^4$ Cr$^{2+}$ cations where the band renormalization is smaller than in BaFe$_2$As$_2$ [22,23]. Additionally, recent electrical resistivity and x-ray diffraction measurements on single and polycrystals of BaCr$_2$As$_2$ under high pressure revealed a tetragonal to collapsed tetragonal (cT) transition at $\sim 18.5$ GPa [25]. The cT phase has also been manifested in CaCo$_{1.86}$As$_2$ at ambient pressure [26] and in CaFe$_2$As$_2$ and SrCo$_2$As$_2$ under high pressures [27,28]. Measurements on isostructural EuCr$_2$As$_2$ containing divalent Eu cations with spin $S = 7/2$ showed this compound to be metallic, with the Cr and Eu sublattices each exhibiting G-type AFM ordering at $T_N = 680(40)$ K and 21.0(1) K, respectively, with the ordered moments on both sublattices aligned along the tetragonal c axis [24,30]. The recent discovery of superconductivity in $M_2$Cr$_3$As$_3$ ($M = $ K, Cs, Rb) under ambient pressure [31,32] and in CrAs under high pressure [33,34] sparked more interest in the search for new Cr-As based compounds.

SrCr$_2$As$_2$ is isostructural to BaCr$_2$As$_2$ [19,20], for which a hint of a magnetic transition at $\sim 165$ K was reported in an early magnetic susceptibility versus temperature study, $\chi(T)$, and attributed to an AFM transi-
II. EXPERIMENTAL DETAILS

A high quality polycrystalline sample (2 g) of SrCr$_2$As$_2$ was synthesized by solid-state reaction using Sr (99.95%), Cr (99.99%) and As (99.999% purity) from Alfa-Aesar. The synthesis was started by reacting small pieces of Sr metal with prereacted CrAs taken in the ratio Sr:Cr:As = 1.05:2. Excess Sr was added in the starting composition to avoid the presence of unreacted CrAs phase and to compensate for Sr loss due to evaporation. The mixture was pelletized, placed in an alumina crucible, and sealed in an evacuated quartz tube. The mixture was placed in a box furnace and heated to 900 °C at a rate of 100 °C/h and held at that temperature for 48 h, then the furnace was cooled to room temperature. This process was repeated twice with intermediate grinding. The resulting material was reground inside a helium-filled glove box, pelletized, and then sealed under 1 atm high purity argon in a quartz tube. The sample was heated to 1150 °C at the rate of 100 °C/h and held there for 48 h following by furnace cooling. Powder x-ray diffraction of the final product confirmed the phase purity of SrCr$_2$As$_2$. The magnetization $M(T)$ measurement in the temperature range 1.8 to 300 K was performed using a Quantum Design Inc., magnetic properties measurement system (MPMS). The high temperature $M(T)$ measurement from 300 to 900 K was performed using the vibrating sample magnetometer (VSM) option of a Quantum Design Inc., physical properties measurement system (PPMS).

Powder neutron diffraction measurements were performed at the thermal triple-axis spectrometer TRIAX at the University of Missouri Research Reactor. Measurements were carried out with an incident energy of 14.7 meV, using Soller slit collimations of 60°-60°-sample-40°-80°. Pyrolytic graphite filters were placed both before and after the sample to reduce higher-order wave-lengths. The pelleted sample of mass $\sim$ 2 g was placed in an Al holder and was mounted on the cold finger (made of Cu) of a cryofurnace to reach temperatures of 12 K $\leq T \leq$ 612 K. Rietveld refinements of the neutron diffraction data were carried out using FullProf software.

III. RESULTS AND DISCUSSION

The temperature dependence of the magnetic susceptibility, $\chi \equiv M/H$, with an applied magnetic field $H = 0.1$ T, is shown in Fig. 2. Over the extended temperature range, $\chi$ increases monotonically. The $\chi(T)$ shows a distinct change in slope around $\sim 600$ K indicative of an AFM transition. We identify the AFM transition temperature $T_N = 600(10)$ K as the peak temperature of a $\lambda$–type anomaly obtained from $d(\chi(T))/dT$ versus $T$ as shown in the inset of Fig. 2. Note that our $\chi(T)$ measurements and the neutron diffraction studies described below are inconsistent with the previous report of Ref. 21, suggesting an AFM transition at $T_N$ $\sim$ 165 K which is evidently due to impurities. At temperatures above $T_N$, the susceptibility appears to approach a broad maximum, indicative of strong two-dimensional AFM correlations setting in well above the ordering temperature, which by virtue of weak AFM interplanar coupling lead to the three dimensional AFM structure observed below $T_N$.

Figures 3(a) and 3(b) show the full powder neutron diffraction pattern obtained at $T = 611$ K ($> T_N$) and $T = 12$ K ($< T_N$), respectively. Notice that all the nuclear and magnetic Bragg peaks coincide as shown in

![Graphical representation](image-url)
TABLE I: Fit parameters obtained from Rietveld refinements of the powder neutron diffraction patterns at the two listed temperatures with tetragonal \( I4/mmm \) space group. \( a \), \( c \), and \( V \) are the unit cell parameters and the unit cell volume, respectively. \( z_{As} \) represents the As \( z \) position in the crystal structure. \( d_{Cr-Cr} \) and \( d_{Cr-As} \) are the in-plane Cr–Cr and Cr–As distances, respectively. \( \chi^2 \) gives the overall value of the goodness of fit. The error (one standard deviation) in the last digit of a quantity is shown in parentheses.

| \( T \) (K) | \( a \) (Å) | \( c \) (Å) | \( c/a \) | \( V \) (Å\(^3\)) | \( z_{As} \) | \( d_{Cr-Cr} \) (Å) | \( d_{Cr-As} \) (Å) | \( \chi^2 \) |
|-------------|-------------|-------------|--------|-----------------|-------------|-----------------|-----------------|--------|
| 12          | 3.9063(8)   | 12.933(4)   | 3.311(1)| 197.35(8)       | 0.3667(7)   | 2.762(6)       | 2.468(3)       | 3.04   |
| 611         | 3.9519(7)   | 12.921(4)   | 3.261(1)| 202.82(8)       | 0.3659(6)   | 2.8015(5)      | 2.483(2)       | 2.90   |

Fig. 3: (Color online) Observed neutron diffraction patterns (red open circles), fits from the Rietveld refinement (black solid lines) and their differences (dark yellow solid lines) at (a) \( T = 611 \) K (\( > T_N \)) and (b) \( T = 12 \) K (\( < T_N \)). The vertical bars are the expected Bragg peak positions as mentioned in the panels. Additional peaks due to the Al sample holder and Cu cold finger were observed and have been taken into account while fitting.

Fig. 4: (Color online) (a) Lattice parameters \( a \) and \( c \) as a function of temperature, \( T \). (b) \( T \)-dependence of the \( c/a \) ratio and unit cell volume \( V \).

Moments arranged antiferromagnetically with all nearest neighbors, both in-plane and out-of-plane, and aligned along the \( c \) axis, as shown in Fig. 1. We note that the value of the ordered moment at \( T = 12 \) K is found to be \( \mu = 1.9(1) \mu_B/\text{Cr} \), where \( \mu_B \) is the Bohr magneton, and is similar to \( \text{BaCr}_2\text{As}_2 \) [22].

The fit parameters from the Rietveld refinements of the diffraction patterns are listed in Table I. The lattice parameter \( a \) and the unit cell volume \( V = a^2c \) decrease by about \( \sim 1.5\% \) and \( 2.5\% \), respectively, between 611 K and 12 K, while the \( c \) lattice parameter increases slightly. This is accompanied by an almost \( \sim 1.5\% \) change in the Cr–Cr distance, compared with \( \sim 0.5\% \) change in the Cr–As distance at the two temperatures.
For temperature dependence measurements, two regions in $2\theta$ were chosen. The first region is centered around the (1 0 1) Bragg peak, $34^\circ \leq 2\theta \leq 39^\circ$, which has a weak nuclear contribution and for which the magnetic signal is the strongest, making it ideal for the temperature dependence of the order parameter. The second region, $46^\circ \leq 2\theta \leq 52^\circ$, covers the (1 0 3) and (1 1 0) Bragg peaks, from which the temperature dependence of the lattice parameters and the unit cell volume were obtained. The lattice parameter $a$ is obtained from the (1 1 0) Bragg peak and is then used to determine the lattice parameter $c$ from the (1 0 3) Bragg peak. Figure 4(a) shows the temperature dependence of the $a$ and $c$ lattice parameters while Fig. 4(b) shows the temperature dependence of the $c/a$ ratio and the unit cell volume $V$. Since we do not have a full diffraction pattern at these temperatures, these are not Rietveld-refined values, but provide a good estimate obtained from the $2\theta$ values of the centers of the fitted Bragg peaks. The $a$ lattice parameter decreases monotonically from high temperatures while the $c$ lattice parameter remains almost constant throughout the measured temperature range with a slight increase with decreasing temperature. The $c/a$ ratio increases with decreasing temperature and becomes almost constant below 200 K while the unit cell volume $V$ decreases monotonically. These results are qualitatively similar to those in BaCr$_2$As$_2$ but distinctly different from those of other SrT$_2$As$_2$ ($T = $ Mn, Fe, Co) compounds. Specifically, SrMn$_2$As$_2$ does not crystallize in a tetragonal $I4/mmm$ space group but forms a trigonal lattice with collinear AFM structure. SrFe$_2$As$_2$ undergoes a first order structural transition from tetragonal to an orthorhombic AFM phase at low temperatures and SrCo$_2$As$_2$ is non-magnetic with $I4/mmm$ crystal symmetry but undergoes a pressure-induced cT phase.

IV. SUMMARY

We have shown that SrCr$_2$As$_2$ exhibits itinerant AFM with a G-type magnetic structure below $T_N = 590(5)$ K.
with the Cr magnetic moments aligned along the c axis. However, strong magnetic correlations develop well above $T_N$ as evident from the susceptibility measurements. We find that the system remains tetragonal in the $I4/mmm$ symmetry down to the base temperature ($\sim 12$ K). The lattice parameter ratio $c/a$ and the ordered magnetic moment $\mu$ saturate at about the same temperature below $\sim 200$ K, indicating a possible magneto-elastic coupling. The derived $\mu = 1.9(1) \mu_B$/Cr is significantly reduced due to the itinerant character of the system, caused by the hybridization between the Cr $3d$ and the As $4p$ orbitals.

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