Article

Structural, Electronic, and Physical Properties of a New Layered Cr-Based Oxyarsenide $\text{Sr}_2\text{Cr}_2\text{AsO}_3$

Yi-Qiang Lin ¹, Hao Jiang ^{1,2}, Hua-Xun Li ¹, Shi-Jie Song ¹, Si-Qi Wu ¹, Zhi Ren ³ and Guang-Han Cao ^{1,4,*}

¹ Department of Physics, Zhejiang University, Hangzhou 310027, China; yiqianglin@zju.edu.cn (Y.-Q.L.); jialay@zju.edu.cn (H.J.); lihuaxun@zju.edu.cn (H.-X.L.); 11936028@zju.edu.cn (S.-J.S.); sqwu@zju.edu.cn (S.-Q.W.)

² School of Physics and Optoelectronics, Xiangtan University, Xiangtan 411105, China

³ School of Science, Westlake Institute for Advanced Study, Westlake University, Hangzhou 310064, China; renzhi@westlake.edu.cn

⁴ Zhejiang Province Key Laboratory of Quantum Technology and Devices, Interdisciplinary Center for Quantum Information and State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, China

* Correspondence: ghcao@zju.edu.cn

Abstract: We report synthesis, crystal structure, and physical properties of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. The new compound crystallizes in a $\text{Sr}_2\text{GaO}_3\text{CuS}$ -type structure with two distinct Cr sites, Cr(1) in the perovskite-like block layers of “ $\text{Sr}_3\text{Cr}_2\text{O}_6$ ” and Cr(2) in the ThCr_2Si_2 -type layers of “ SrCr_2As_2 ”. An inter-block-layer charge transfer is explicitly evidenced, which dopes electrons in the CrO_2 planes and simultaneously dopes holes into the CrAs layers. Measurements of electrical resistivity, magnetization, and specific heat, in combination with density-functional theoretical calculations, indicate that the title material is an antiferromagnetic metal. The Cr(2) magnetic moments in the CrAs layers order at 420 K, while the Cr(1) spins in the CrO_2 planes show quasi-two-dimensional magnetism with long-range ordering below 80 K. Both Néel temperatures are significantly reduced, compared with those of the cousin material $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$, probably due to the intrinsic charge-carrier doping. Complex re-entrant magnetic transitions with a huge magnetic hysteresis were observed at low temperatures.

Keywords: Cr-based oxyarsenide; physical properties; DFT calculations; antiferromagnetism; inter-layer charge transfer

Citation: Lin, Y.-Q.; Jiang, H.; Li, H.-X.; Song, S.-J.; Wu, S.-Q.; Ren, Z.; Cao, G.-H. Structural, Electronic, and Physical Properties of a New Layered Cr-Based Oxyarsenide $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. *Materials* **2022**, *15*, 802. <https://doi.org/10.3390/ma15030802>

Academic Editor: Andres Sotelo

Received: 8 December 2021

Accepted: 17 January 2022

Published: 21 January 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The discoveries of superconductivity in CrAs [1,2] at high pressures and, later in quasi-one-dimensional $\text{A}_2\text{Cr}_3\text{As}_3$ ($A = \text{K}, \text{Rb}, \text{Cs}$) at ambient pressure [3–5], motivate the research interest in other Cr-based materials [6–16]. Of particular interest are those with CrAs layers [17–20], which resemble the FeAs layers in iron-based superconductors [21]. Similar to the parent compounds of iron-based superconductors, these CrAs-layer based materials, such as BaCr_2As_2 [18] and LaCrAsO [20], also show antiferromagnetic (AFM) order and metallic conduction. Theoretical studies [6–8] suggest possible superconductivity in doped BaCr_2As_2 and LaCrAsO . Notably, the Néel temperatures are as high as ~ 600 K (see Table 1), suggesting a large magnetic exchange interaction. If the AFM order can be suppressed, according to the common features of unconventional superconductivity [22], one expects possible high-temperature superconductivity in the class of Cr-based materials. In this context, explorations for additional materials with CrAs layers are of significance [23–26].

In 2015, the present authors [23] succeeded in synthesizing a Cr-based oxyarsenide $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$. Structurally, the compound can be viewed as an intergrowth of ThCr_2Si_2 -type SrCr_2As_2 and perovskite-like infinite-layer “ SrCrO_2 ” [27], thus bearing both CrAs layers and CrO_2 planes. The material was demonstrated to be an AFM correlated metal. Later, the neutron diffraction study [28] revealed that the magnetic moments of Cr(1) (in

the CrO₂ planes) and Cr(2) (in the CrAs layers) are 3.10(6) μ_B and 2.19(4) μ_B , respectively. The Cr(1) spins form a La₂CuO₄-like AFM order at 291 K, and the Cr(2) moments show a C-type (Néel-type antiferromagnetism in the *ab* plane and ferromagnetism along the *c* axis) AFM order below 590 K.

Table 1. Comparison of structural (at room temperature) and physical properties of the compounds with CrAs layers and/or CrO₂ planes. h_{CrAs} denotes the As height from the Cr plane. $\alpha_{\text{As-Cr-As}}$ is the As-Cr-As bond angle along *a* or *b* direction. BVS is the bond valence sum of Cr(1) coordinated by five oxygen atoms. T_{N1} and T_{N2} are the antiferromagnetic transition temperatures associated with Cr(1) and Cr(2), respectively, and μ_{Cr1} and μ_{Cr2} are their saturation magnetic moments. The symbol “-” represents that those data are not available.

Compounds	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>	h_{CrAs} (Å)	$\alpha_{\text{As-Cr-As}}$ (°)	BVS	T_{N1} (K)	μ_{Cr1} (μ_B)	T_{N2} (K)	μ_{Cr2} (μ_B)	Refs.
BaCr ₂ As ₂	3.9678(4)	13.632(3)	3.436	1.513	105.3	-	-	-	-	-	[18]
BaCr ₂ As ₂	3.9667	13.6214	3.434	1.512	105.4	-	-	-	580	1.9	[9]
SrCr ₂ As ₂	3.918(3)	13.05(1)	3.331	1.449	107.0	-	-	-	590 [11]	1.9(1)	[17]
EuCr ₂ As ₂	3.893(2)	12.872(2)	3.306	1.455	106.5	-	-	-	680 [29]	1.7(4)	[19]
LaCrAsO	4.0412(3)	8.9863(7)	2.224	1.460	108.3	-	-	-	>300	-	[20]
Sr ₂ Cr ₃ As ₂ O ₂	4.0079(1)	18.8298(3)	4.698	1.505	106.2	2.10	291	2.97 (calc.)	-	2.59 (calc.)	[27]
Sr ₂ Cr ₃ As ₂ O ₂	4.00671(6)	18.8310(5)	4.700	1.503	106.2	1.90	291	3.10(6)	590	2.19(4)	[28]
Sr ₂ Cr ₃ As ₂ O ₂	4.00800(2)	18.8214(1)	4.696	1.505	106.4	1.90	330	3.34(1)	600	2.68(1)	[25]
Ba ₂ Cr ₃ As ₂ O ₂	4.05506(2)	20.5637(1)	5.071	1.478	107.8	1.79	230	3.30(1)	465	2.23(1)	[25]
Sr ₂ CrFeAsO ₃	3.9112(1)	15.7905(3)	4.037	-	-	2.69	31	-	-	-	[30]
Sr ₂ CrFeAsO ₃	3.918	15.683	4.003	-	-	2.93	-	-	-	-	[31]
Sr ₂ ScCrAsO ₃	4.043(9)	16.038(1)	3.967	1.498	106.9	-	-	-	-	-	[26]
Sr ₂ Cr ₂ AsO ₃	3.9087(2)	16.0481(4)	4.300	1.560	102.8	2.52	80	2.52 (calc.)	420	2.41 (calc.)	This work

We note that the perovskite-like block layer A₃Cr₂O₆ (*A* = Sr, Ba) can be intergrown with the ThCr₂Si₂-type AM₂As₂ (*M* = Fe, Co) [30,31], forming a Sr₂GaO₃CuS-type structure [32]. This suggests the possibility of synthesis of an analogous Cr-based oxyarsenide, Sr₂Cr₂AsO₃, which contains alternating layers of “Sr₃Cr₂O₆” and “SrCr₂As₂” (see the inset of Figure 1). Notably, the target structure bears distinct Cr valence in different block layers (namely, Cr³⁺ in the perovskite-like A₃Cr₂O₆ and Cr²⁺ in SrCr₂As₂), in contrast to the case in Sr₂Cr₃As₂O₂ where the valences of Cr(1) and Cr(2) are both 2+. An inter-block-layer charge transfer is thus anticipated, which effectively dopes holes in the CrAs layers. This makes Sr₂Cr₂AsO₃ particularly interesting.

In this paper, we report the synthesis, crystal structure, and physical properties of Sr₂Cr₂AsO₃ (this phase was identified using electron microscopy as an impurity (1.3%) in the synthesized sample of Sr₂Cr₃As₂O₂ [25]). The crystal structure is determined by the Rietveld refinement, from which the bond-valence sum of Cr(1) is calculated to be +2.52. The result indicates a mixed valence for Cr(1), suggesting an inter-block-layer charge transfer. The charge transfer is also supported by the Cr(1) effective moment from the magnetic measurement and the Bader charge analysis on the basis of density-functional-theory (DFT) calculations. The magnetic measurement reveals that the Néel temperatures in the CrAs layers and the CrO₂ planes are $T_{\text{N2}} = 420$ K and $T_{\text{N1}} \approx 80$ K, which are remarkably reduced, in comparison with the counterparts (~ 600 K and ~ 300 K, respectively) in Sr₂Cr₃As₂O₂. The suppression of the Néel temperatures is probably due to the charge-carrier dopings, originating from the interlayer charge transfer. Complex re-entrant magnetic transitions with a huge magnetic hysteresis were observed at low temperatures. The magnetic ground state is studied by the DFT-based first-principles calculations.

Figure 1. Powder X-ray diffraction at room temperature and its Rietveld refinement profile of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. The inset shows the crystal structure consisting of block layers of $\text{Sr}_3\text{Cr}_2\text{O}_6$ and SrCr_2As_2 .

2. Experimental Methods

The $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ polycrystalline sample was synthesized by solid-state reactions in vacuum. The source materials were Sr pieces (99%), As pieces (99.999%), Cr powders (99.99%), and Cr_2O_3 powders (99.97%). Mixtures of these raw materials with the nearly nominal composition (the oxygen content is reduced by 6% to compensate the slight oxidation in the reactive Sr pieces) were put into an alumina crucible, sealed in an evacuated silica tube, then calcined in a muffle furnace at 800 °C for 24 h. After cooling, the sample was thoroughly ground for homogenization and pressed into a pellet in a glove box filled with argon gas. The pellet was also loaded an alumina crucible, sealed in an evacuated silica tube, and then heated to 1100 °C, holding at this temperature for 40 h. Finally, the sample was allowed to cool down by switching off the furnace.

The X-ray diffraction (XRD) was performed at room temperature using a PANalytical X-ray diffractometer with $\text{Cu-K}\alpha_1$ radiation. The crystal structure was refined by the Rietveld analysis using FullProf suite [33]. The electrical resistivity and specific heat were measured with a quantum design physical property measurement system (PPMS). The magnetic properties were measured by a quantum design magnetic property measurement system (MPMS-3). The measurement was allowed at temperatures up to 700 K by employing a high-temperature option.

The first-principles calculations were done within the generalized gradient approximation [34] by using the Vienna Ab-initio Simulation Package (VASP) [35]. The experimental crystal structure was used for the calculations. The plane-wave basis energy cutoff was chosen to be 550 eV. A $10 \times 10 \times 5$ Γ -centered K-mesh was used for the density-of-states (DOS) calculations.

3. Results and Discussion

3.1. Crystal Structure

Figure 1 shows the XRD pattern of the as-prepared polycrystalline sample of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. All the strong XRD reflections can be indexed using a primitive tetragonal unit cell with $a \approx 3.91$ Å and $c \approx 16.05$ Å. Some unindexed weak peaks probably come from the unreacted CrAs and SrO, while the others cannot be identified with known phases. The lattice constants are very close to those of the analogous compound $\text{Sr}_2\text{CrFeAsO}_3$ [30,31], suggesting the formation of the target phase. Indeed, the XRD data can be successfully

refined with the $\text{Sr}_2\text{GaO}_3\text{CuS}$ -type structure model [32]. The R factors of the refinement are $R_B = 4.65\%$ and $R_{wp} = 8.21\%$. Furthermore, the Goodness-of-fit index is 3.8. The refined crystallographic data are listed in Table 2.

Table 2. Room-temperature crystallographic data of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ with lattice parameters of $a = 3.9087(2)$ Å and $c = 16.0481(4)$ Å, and with space group $P4/nmm$ (No. 129).

Atoms	Sites	x	y	z	$B(\text{\AA}^2)$
Sr(1)	$2c$	0.75	0.75	0.1997(3)	0.56
Sr(2)	$2c$	0.75	0.75	0.4177(3)	0.90
Cr(1)	$2c$	0.25	0.25	0.3117(4)	0.81
Cr(2)	$2a$	0.25	0.75	0	0.61
As	$2c$	0.25	0.25	0.0973(3)	0.36
O(1)	$4f$	0.25	0.75	0.2945(10)	1.01
O(2)	$2c$	0.25	0.25	0.4411(16)	0.73

As shown in the inset of Figure 1, the crystal structure of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ can be viewed as an alternating stacking of $\text{Sr}_3\text{Cr}_2\text{O}_6$ and SrCr_2As_2 block layers along the c direction. According to the block-layer model for an intergrowth structure [36], inter-block-layer charge transfer and lattice match are the two major factors for the stabilization. Furthermore, the lattice constant a is mainly determined by the structural block with a larger stiffness. In Table 1, one sees that the a axis of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ is close to that of $\text{Sr}_2\text{CrFeAsO}_3$, but significantly smaller than those of $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$ and $\text{Sr}_2\text{ScCrAsO}_3$. The result suggests that the perovskite-like block layers of $\text{Sr}_3\text{Cr}_2\text{O}_6$, SrCrO_2 , and $\text{Sr}_3\text{Sc}_2\text{O}_6$ are harder, which dominantly determine the a axis. Note that the a axis of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ is also close to that of SrCr_2As_2 , which indicates a very good lattice match between the two building blocks.

There are two distinct crystallographic Cr sites, Cr(1) and Cr(2), in the block layers of $\text{Sr}_3\text{Cr}_2\text{O}_6$ and SrCr_2As_2 , respectively. The former is pyramidally coordinated by five oxygen atoms with a formal valence of +3, and the latter is bonded tetrahedrally by four As atoms with a formal valence of +2. To evaluate the possible inter-block-layer charge transfer, we calculate the bond valence sum (BVS) [37] of Cr(1) (note that the BVS concept does not apply for Cr(2) because of the dominant covalence of the Cr(2)–As bonding). The calculated BVS value is calculated to be +2.52, suggesting a mixed valence for Cr(1). In comparison, the Cr-BVS value in $\text{Sr}_2\text{CrFeAsO}_3$ is 2.93 [31], and it is 1.9–2.1 in $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$ [23,25,28]. All these data conformably suggest an interlayer charge transfer between the two block layers, which primarily stabilizes the structure [36]. The interlayer charge transfer leads to electron doping in the CrO_2 planes and hole doping in the CrAs layers. From Table 1, one sees that the As height (above the Cr plane) is exceptionally high and, correspondingly, the As–Cr–As bond angle along a axis is exceptionally small. These structural changes may be associated with the effective hole doping in the CrAs layers.

3.2. Electrical Resistivity

The temperature dependence of resistivity, $\rho(T)$, for the $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ polycrystalline sample is shown in Figure 2. A typical metallic behavior shows up without any obvious anomaly below room temperature. Similar observations were observed in BaCr_2As_2 [9,18] and LaCrAsO [20]. For $\text{Sr}_2\text{ScCrAsO}_3$ and $\text{Ba}_2\text{ScCrAsO}_3$ [26], which contain insulating block layers of $\text{Sr}_3\text{Sc}_2\text{O}_6$ and $\text{Ba}_3\text{Sc}_2\text{O}_6$, respectively, the $\rho(T)$ behaviors are basically metallic. These results suggest that the CrAs layers are mainly responsible for the metallic conduction.

Figure 2. Temperature dependence of electrical resistivity of the $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ polycrystalline sample. The solid line is a fit with the extended Bloch-Grüneisen formula (see the text). The inset shows the difference, $\Delta\rho$, between the experimental and fitted data. The drop in $\Delta\rho$ by $\sim 3\%$ below 70 K suggests reduction of the magnetic scattering by Cr(1) spins.

As treated previously [23], the $\rho(T)$ data were fitted with the extended Bloch-Grüneisen formula,

$$\rho(T) = \rho_0 + A\left(\frac{T}{\Theta_R}\right)^n \int_0^{\Theta_R/T} \frac{x^n}{(e^x - 1)(1 - e^{-x})} dx, \quad (1)$$

where n is a fitting parameter characterizing the conduction electron scattering [38–40]. The data fitting yields $n = 2.58$, $\Theta_R = 303$ K, and $\rho_0 = 2.87$ mΩ cm. One sees that the n value lies in between 2 and 3, implying both electron-electron and electron-magnon scattering [39,41]. To reveal the possible change in magnetic scattering, we made the subtraction of fitted data from the experimental ones. The result is plotted in the inset of Figure 2. One sees a broad dip (resistivity decreased by $\sim 3\%$) below ~ 70 K. This slight response of resistivity could be associated with the magnetic ordering at the Cr(1) site (see below).

3.3. Magnetic Properties

Figure 3 shows the temperature dependence of magnetic susceptibility, $\chi(T)$, for $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. The data show a Curie-Weiss (CW) behavior at high temperatures up to 700 K. The CW behavior is reasonably attributed to the contribution of Cr(1) in the $\text{Sr}_3\text{Cr}_2\text{O}_6$ layers, because the $\chi(T)$ of materials with CrAs layers only, such as BaCr_2As_2 [9], LaCrAsO [20], and $\text{Sr}_2\text{ScCrAsO}_3$ [26], is not CW like. The data fitting in the temperature range from 314 K to 700 K by using the extended CW law, $\chi = \chi_0 + C/(T + \theta_{\text{CW}})$, yields $\chi_0 = 3.15 \times 10^{-4}$ emu mol $^{-1}$, $C = 2.13$ emu K mol $^{-1}$, and $\theta_{\text{CW}} = 352$ K. The positive CW temperature indicates dominant antiferromagnetic interactions among the Cr(1) spins. The fitted parameter C gives rises to an effective moment for Cr(1) atoms, $\mu_{\text{eff}}^{\text{Cr1}} = 4.13 \mu_B$, which lies in between the expected values of high-spin Cr^{3+} ($3.87 \mu_B$) and high-spin Cr^{2+} ($4.90 \mu_B$). The result suggests local-moment and mixed-valence scenarios for Cr(1) atoms. The latter arises from the interlayer charge transfer as demonstrated above.

Figure 3. Temperature dependence of magnetic susceptibility, $\chi(T)$, under an applied field of $\mu_0 H = 3$ T for $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. The green solid line is the Curie-Weiss (CW) fit. The upper inset plots the difference in χ between the experimental data and the fitted ones. The bottom inset shows the closeup of the $\chi(T)$ curves at low temperatures.

To detect the possible magnetic transition related to the CrAs layers in $\text{Sr}_2\text{Cr}_2\text{AsO}_3$, we treated the CW magnetism as a background, and made a subtraction of the CW-fit data from the experimental $\chi(T)$ data. As is seen in the upper-right inset of Figure 3, a drop of χ shows up at 420 K, indicating an AFM transition. Here we note that the Néel temperature of the Cr(2) sublattice, T_{N2} , is remarkably reduced, compared with those of other CrAs-layer based materials including SrCr_2As_2 (see Table 1). Since the a axes of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ and SrCr_2As_2 are comparable, the reduction of T_{N2} in $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ is arguably attributed to the hole-doping effect in the CrAs layers because of the interlayer charge transfer.

Now that the high-temperature CW behavior comes from the Cr(1)-spin paramagnetism, the susceptibility drop below $T_{N1} \approx 80$ K in Figure 3 is then ascribed to an AFM ordering in $\text{Sr}_3\text{Cr}_2\text{O}_6$ block layers. The slight loss of resistivity below ~ 70 K in Figure 2 can be understood in terms of reduction of magnetic scattering. The T_{N1} value is remarkably lower than $\theta_{CW} = 352$ K, implying quasi-two-dimensional (quasi-2D) magnetism. Indeed, there is a broad hump above T_{N1} , reflecting quasi-2D AFM correlations/short-range order [42–45]. Similar behaviors also appear in $\text{Sr}_3\text{Cr}_2\text{O}_6$ -layer-bearing $\text{Sr}_2\text{CrO}_3\text{FeAs}$ [31] and $\text{Sr}_2\text{CrO}_3\text{CuS}$ [46]. Besides, the reduced T_{N1} (in comparison with that of $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$ [25,28]) may be accounted for by the electron doping in the CrO_2 planes.

Interestingly, there exist additional magnetic anomalies at lower temperatures, which are shown in the bottom-left inset of Figure 3. More data at varied magnetic fields are given in Figure 4. One sees that, below T_{N1} , the magnetic susceptibility increases steeply with decreasing temperature at T_R , suggesting a re-entrant magnetic transition. With further decreasing temperature, the FC and ZFC data bifurcates at T_B , and χ_{ZFC} drops abruptly below T_B . The inset of Figure 4b plots T_R and T_B as functions of magnetic field. It is clear that T_R increases steadily with field, while T_B decreases slowly.

Figure 4. Temperature dependence of magnetic susceptibility for $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ at varied magnetic fields of 0.1, 1, 5 (a), 6, and 7 T (b) in the field-cooling (FC) and zero-field-cooling (ZFC) measurement modes. The inset of (b) shows the changes of T_R and T_B with the magnetic field.

In order to clarify the magnetic anomalies above, we carried out the measurements of isothermal magnetization, $M(H)$, by sweeping magnetic fields in a loop (i.e., $\mu_0 H = 0 \text{ T} \rightarrow 6 \text{ T} \rightarrow -6 \text{ T} \rightarrow 6 \text{ T}$). Figure 5 displays some selective $M(H)$ data. At first sight, M seems to be linearly proportional to H at varied temperatures from 2 K to 300 K. On closer examination, however, a slight magnetic hysteresis can be found. To extract the hysteresis, we made a subtraction, $\Delta M = M - M_{\text{ref}}$, by employing a paramagnetic reference of $M_{\text{ref}} = 41.5 H$. As a result, an anomalous hysteresis shows up in the ΔM plot [Figure 5b]. In the low-field region, one sees a ferromagnetic-like magnetization with a coercive field of about 0.018 T (180 Oe). This reflects that the re-entrant magnetic transition at T_R induces a ferromagnetic component. Nevertheless, the “saturation” magnetization is only about 5 emu/mol, equivalent to $\sim 10^{-3} \mu_B$ per formula unit. Given the antiferromagnetic states in both Cr(2) and Cr(1) sublattices, then, the small-moment ferromagnetism is likely originated from the Cr-spin canting. The origin of the spin canting could be in relation with double exchange, as shown in the classical literature by de Gennes [47]. Notably, the magnetic hysteresis is huge, consistent with the bifurcation of magnetic susceptibility in FC and ZFC measurements under magnetic fields up to $\mu_0 H = 7 \text{ T}$. Furthermore, the magnetic hysteresis does not form a loop when increasing field from -6 to 6 T . This magnetic behavior is rarely seen. We conjecture that it is due to the complex magnetic structure and, in particular,

in relation with the proximity of magnetic energy for different spin directions (see the DFT-based calculations below).

Figure 5. (a) Field dependence of magnetization at some selective temperatures for $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. Panel (b) shows the magnetization difference, $\Delta M = M - 41.5H$, at 2 and 10 K. All the insets are closeups for showing the details clearly.

3.4. Specific Heat

Figure 6 shows the temperature dependence of specific heat, $C(T)$, for $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. At first sight, there is no obvious anomaly below room temperature. That is to say, the AFM transition below 80 K, manifested by the magnetic measurement above, is not associated with an abrupt change in entropy. This is actually consistent with the quasi-2D magnetism, in which magnetic correlations and short-range magnetic order exist at a wide temperature range around T_{N1} .

Let us first analyze the low-temperature $C(T)$ data. At such low temperatures below 5 K, the lattice contribution well obeys Debye's T^3 law. Furthermore, the magnetic contributions can be ignored because $T \ll T_N$. Therefore, the total specific heat can be formulated with $C(T) = \gamma T + \beta T^3$, where γ is the electronic specific-heat coefficient. The upper inset of Figure 6 plots C/T as a function of T^2 in the low temperature range from 2 to 5 K. Indeed, one sees that C/T is essentially linear with T^2 . The linear fitting gives $\gamma = 13.05 \text{ mJ K}^{-2} \text{ mol}^{-1}$ and $\beta = 0.517 \text{ mJ K}^{-4} \text{ mol}^{-1}$. Using the formula $\Theta_D = [(12/5)NR\pi^4/\beta]^{1/3}$, we

obtain a Debye temperature of 311.0 K. The Θ_D value is rather close to Θ_R obtained from the fit of resistivity above.

Figure 6. Temperature dependence of specific heat for $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. The upper inset shows the low-temperature specific-heat data, plotted with C/T vs. T^2 . The lower inset plots $\Delta C/T$ (left axis) and the magnetic entropy (right axis) as functions of temperature (see text for the details).

Now we analyze the whole $C(T)$ data, in order to extract the possible magnetic contribution from Cr(1) spins. Here, the magnetic contribution from Cr(2) can be ignored, because T_{N2} is well above room temperature. Then, similar to our previous treatment [23], the non-magnetic contribution of specific heat can be expressed by:

$$C = \xi C_D + (1 - \xi) C_E + \gamma T, \quad (2)$$

where $C_D = 9NR(\frac{T}{\Theta_D})^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$ and $C_E = 3NR(\frac{\Theta_E/T}{e^{\Theta_E/T} - 1})^2 e^{\Theta_E/T}$ represent the lattice contributions in terms of Debye and Einstein models, respectively. The coefficients, ξ and $(1 - \xi)$, describe their individual weights. With γ and Θ_D fixed ($13.05 \text{ mJ K}^{-2} \text{ mol}^{-1}$ and 311.0 K , respectively), only two adjust parameters, ξ and Θ_E , were fitted. The data in the range of $10 \leq T \leq 200 \text{ K}$ were dropped in the fitting, because the magnetic contribution cannot be ignored there. As a result, $\Theta_E = 668.7 \text{ K}$ and $\xi = 0.616$ were yielded. The high Θ_E value is consistent with the lattice vibrations associated with light (oxygen) atoms and, accordingly, the fitted ξ value is very close to the fraction of heavy-element atoms ($5/8$).

With the fitted data C_{fit} , the magnetic contribution from Cr(1) spins can be evaluated by the subtraction, $C_m^{\text{Cr1}} \approx \Delta C = C_{\text{exp}} - C_{\text{fit}}$. The lower inset of Figure 6 plots the temperature dependence of the resulted $\Delta C/T$. The main peak appears below $T_{N1} = 80 \text{ K}$, which is consistent with the magnetic susceptibility measurement. One also sees a long tail extending to $\sim 200 \text{ K}$, indicative of magnetic contributions well above T_{N1} . This corroborates quasi-2D magnetic correlations/short-range order in the system. The magnetic entropy, S_m , can be obtained by the integral $\int_0^T \frac{C_m}{T} dT$, and the resulted S_m is $9.1 \text{ J K}^{-1} \text{ mol}^{-1}$, which is slightly smaller, yet reasonably close to, the expected value of $R \ln(2S + 1) = 11.5 \text{ J K}^{-1} \text{ mol}^{-1}$ (here $S = 3/2$ is taken). The result is supported by the theoretical calculations below which shows an ordered moment of $2.52 \mu_B$ for Cr(1).

3.5. First-Principles Calculations

The possible magnetic ground state of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ was investigated by the DFT-based first-principles calculations. Owing to the complicated crystal structure with both CrO_2 planes and CrAs layers, we did not calculate all the combinations of Cr-spin orderings.

In stead, we took two steps to find out the possible magnetic ground state. First, we focused on the magnetic structure associated with Cr(2) moments, assuming that Cr(1) is non-spin-polarized. This is because the magnetic exchange interactions in the Cr(2) subsystem are expected to be larger due to the higher T_{N2} value and, indeed, there is a temperature window which shows AFM order for Cr(2) and paramagnetism for Cr(1) [25,28]. Second, the whole magnetic structure was optimized by switching on the local spins of Cr(1). The spin directions were chosen along the crystallographic axes, according to the experimental results of the related compounds [9,11,20,25,28,29].

Table 3 lists the Cr moments as well as the magnetic energy E_m relative to the non-magnetic state for different magnetic structures of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. The first six rows show the results with non-magnetic Cr(1). Clearly, the in-plane Néel-type antiferromagnetism in the Cr(2) sublattice shows the lowest magnetic energy. Cr spins tend to align along the c axis. Furthermore, G- and C-type AFM configurations have almost the same magnetic energy (within the calculation accuracy), indicating a very weak interlayer magnetic coupling and, therefore, both magnetic structures are possible. Experimentally, the G-type AFM order exists in BaCr_2As_2 [9], SrCr_2As_2 [11], EuCr_2As_2 [29], and LaCrAsO [20]. Nevertheless, the C-type AFM order is manifested by $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$ [25,28] and $\text{Ba}_2\text{Cr}_3\text{As}_2\text{O}_2$ [25] in which the distance between CrAs layers is elongated. We thus anticipate that the C-type order is more likely in $\text{Sr}_2\text{Cr}_2\text{AsO}_3$.

Table 3. Calculated magnetic energy E_m (in meV/f.u.) relative to non-magnetic (N) state and the corresponding magnetic moment μ_{Cr} (in μ_B) of different magnetic structures of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. F, S, C, and G denote ferromagnetic, striped AFM, C-type AFM, and G-type AFM structures, respectively. The subscripts ab and c tell the spin directions.

Magnetic Structure	E_m	$\mu_{\text{Cr}(1)}$	$\mu_{\text{Cr}(2)}$
Cr(1)N–Cr(2)N	0	0	0
Cr(1)N–Cr(2)F	−67.9	0	1.726
Cr(1)N–Cr(2)S	−0.5	0	0.078
Cr(1)N–Cr(2) C_{ab}	−310.9	0	2.400
Cr(1)N–Cr(2) C_c	−311.3	0	2.401
Cr(1)N–Cr(2) G_c	−311.1	0	2.401
Cr(1)F–Cr(2) C_c	−911.2	2.653	0.013
Cr(1)F–Cr(2) C_{ab}	−911.2	2.653	0.013
Cr(1)S–Cr(2) C_c	−987.3	2.590	1.085
Cr(1)S–Cr(2) C_{ab}	−1144.4	2.206	0.567
Cr(1) C_c –Cr(2) C_{ab}	−1242.8	2.529	2.417
Cr(1) C_{ab} –Cr(2) C_c	−1249.5	2.521	2.407
Cr(1) C_{ab} –Cr(2) C_{ab}	−1251.0	2.522	2.408
Cr(1) C_c –Cr(2) C_c	−1251.7	2.522	2.409
Cr(1) G_c –Cr(2) C_c	−1252.0	2.522	2.409

The last nine rows in Table 3 present the calculated data for magnetic structures with the C-type magnetic order in CrAs layers. One can find that the Cr(1) spins also favor an in-plane Néel-type antiferromagnetism with collinear configuration. The Cr-spin direction parallel to c axis is mostly stabilized. Nevertheless, the G-type spin order is slightly favored over the C-type one, although the energy difference is quite small. Note that a similar G-type order appears in $\text{Sr}_3\text{Cr}_2\text{O}_7$ with CrO_2 bilayers [48]. Figure 7 depicts the variations of magnetic energy for different magnetic configurations. The most probable magnetic ground

state is predicted to be a G/C-type AFM for Cr(1) and a C-type AFM for Cr(2) with spins along the c axis. The prediction resembles the experimental results in $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$ [25,28] and $\text{Ba}_2\text{Cr}_3\text{As}_2\text{O}_2$ [25].

Figure 7. Calculated magnetic energies for the antiferromagnetic states with different spin directions in Cr(1) (**top** and **bottom**) and Cr(2) (**middle**) sites of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$.

The ordered moments of Cr(1) and Cr(2) are calculated to be 2.52 and 2.41 μ_B , respectively. One notes that the magnetic moment of Cr(1) is reduced by $\sim 0.5 \mu_B$, compared with the Cr(1) moment of 3.10 μ_B (experimental value [28]) and 2.97 μ_B (theoretical result [23]) in $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$. In the ionic limit, the Cr(1) moment in the high-spin state would be $\mu_{\text{Cr}} = gS = 4$ (3) μ_B for Cr^{2+} (Cr^{3+}) in $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$ ($\text{Sr}_2\text{Cr}_2\text{AsO}_3$), if there were no inter-layer charge transfer. The reduction of Cr(1) moment by $\sim 0.5 \mu_B$ dictates the mixed-valence state as demonstrated above.

To evaluate the charge transfer further, we also performed calculations of the Bader valence charges for different elements in $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$ and $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. The results are presented in Table 4. First, the cations of Sr and Cr have less charges, while the anions of As and O have more charges, compared with corresponding neutral atoms. Second, the Bader charges of the cations (anions) decrease (increase) from $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$ to $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. In particular, the Bader charge of Cr(1) decreases by 0.6, suggesting a mixed-valence state for Cr(1). On the other hand, the Bader charge of Cr(2) also decreases significantly, consistent with a hole doping in the CrAs layers.

Table 4. Bader charges of different elements in the magnetic ground states of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$ (2213) and $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$ (2322).

Element	Bader Charge			Neutral
	Q_{2213}	Q_{2322}	$Q_{2213} - Q_{2322}$	
Sr	8.518	8.706	−0.188	10
Cr(1)	10.407	11.011	−0.604	12
Cr(2)	11.396	11.619	−0.223	12
As	16.282	16.012	0.27	15
O	7.300	7.157	0.143	6

Figure 8 shows the energy dependence of electronic density of states (DOS) for the C-type AFM state in $\text{Sr}_2\text{Cr}_2\text{AsO}_3$. Both the projected DOS to each element and the total DOS are presented. One sees that the Cr atoms dominantly contribute the DOS at around the

Fermi energy (E_F). Meanwhile, the hybridizations between Cr-3d and O-2p and between Cr-3d and As-4p are not negligible (O-2p and As-4p contribute 12% and 3% of the total DOS, respectively). Overall, the DOS profile is quite similar to that of $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$ [23]. The bare DOS at the Fermi level is $N(E_F) = 4.08 \text{ eV}^{-1} \text{ f.u.}^{-1}$ based on both spin directions. With the formula of $\gamma_0 = \frac{1}{3}\pi^2 k_B^2 N(E_F)$, we get $\gamma_0 = 11.3 \text{ mJ K}^{-2} \text{ mol}^{-1}$. The γ_0 value is close to the electronic specific-heat coefficient above ($\gamma = 13.05 \text{ mJ K}^{-2} \text{ mol}^{-1}$), suggesting relatively weak electron correlations.

Figure 8. Energy dependence of total and partial electronic density of states (DOS) of the C-type antiferromagnetic state of $\text{Sr}_2\text{Cr}_2\text{AsO}_3$.

As the Cr-3d electrons dominate the states at around E_F , the DOS was then projected to each 3d orbitals. Figure 9 shows the projected DOS with spin up (positive DOS) and spin down (negative DOS). The contributions of d_{xz} and d_{yz} orbitals are almost degenerate and, for simplicity, the data are combined. For Cr(1) in the CrO_2 planes, $d_{x^2-y^2}$ and d_{z^2} orbitals are almost unoccupied (the DOS weights below -2 eV are due to the $d-p$ hybridizations). By contrast, the $d_{yz/xz}$ and d_{xy} orbitals are almost single occupied, which gives rise to a magnetic moment close to $3 \mu_B$. The projected DOS at E_F is mostly contributed from d_{xy} orbital. The result can be roughly understood in terms of ionic crystalline electric field (CEF) splitting. Cr(1) ions are coordinated by five oxygen anions, forming a square pyramid. Under this CEF, the $d_{x^2-y^2}$ and d_{z^2} orbitals are lifted up, thus no electrons fill the two orbitals. On the other hand, the other three orbitals are half filled (see the inset of Figure 9a). One sees that these $d_{xy/yz/xz}$ -orbital-related bands are very narrow, suggesting that the Cr(1) magnetism is basically localized.

The Cr(2) atoms in the CrAs layers are coordinated by four arsenic atoms, forming a tetrahedron. The CEF splitting leads to the lift for $d_{xy/yz/xz}$ orbitals. Nevertheless, these three orbitals strongly hybridize with As-4p electrons, which makes the orbitals effectively occupied with less spin polarizations. On the other hand, the $d_{x^2-y^2}$ and d_{z^2} appear to be basically half filled, which predominately contributes the magnetic moments. The projected DOS at E_F for Cr(2) mostly comes from the $d_{x^2-y^2}$ and $d_{yz/xz}$ orbitals. Like the case in other CrAs-layer based materials, the magnetism in the CrAs layers is largely itinerant.

Figure 9. Projected density of states of 3d orbitals of the Cr(1) at (1/4, 1/4, 0.3116) (a) and Cr(2) at (1/4, 3/4, 0) (b) sites in the C-type antiferromagnetic state of Sr₂Cr₂AsO₃. The insets show the coordinations of Cr(1) and Cr(2) and their corresponding crystalline field splittings.

4. Concluding Remarks

In summary, we have synthesized a novel Cr-based oxyarsenide Sr₂Cr₂AsO₃, which is comprehensively studied by the structural determination, physical-property measurements, and the first-principles calculations. The new material is an intergrowth of perovskite-like “Sr₃Cr₂O₆” and ThCr₂Si₂-type SrCr₂As₂, containing both CrO₂ planes and CrAs layers. Thus, like the cousin compound Sr₂Cr₃As₂O₂, the material bears structural similarities with cuprate and iron-based high-temperature superconductors. Of particular interest in the material is that the Cr atoms in the two block layers show different formal valences. As a result, an inter-block-layer charge transfer is realized, which effectively dopes holes (electrons) in the CrAs (CrO₂) layers. Such a charge-carrier doping is argued to be the main cause for the reduced T_{N2} and T_{N1} . If the AFM Néel temperature in the CrAs layers can be further suppressed by chemical doping and/or applying high pressures, one would expect realization of superconductivity in the system according to the common thread of unconventional superconductors [22].

The title material is demonstrated to be an AFM metal with relatively weak electron correlations. While its CrAs layers show an AFM order at $T_{N2} = 420$ K, the CrO₂ planes exhibit a quasi-2D magnetism with long-range spin ordering below $T_{N2} = 80$ K. At low

temperatures, a re-entrant magnetic transitions with a huge magnetic hysteresis shows up, reflecting complex interactions among Cr(1) and Cr(2) spins and conduction electrons. Our first-principles calculations predict C-type AFM order in the CrAs layers together with C- or G-type AFM order in the CrO₂ planes. Future study with neutron diffraction is called for to verify the magnetic structure and to clarify the re-entrant magnetic transition.

Author Contributions: Conceptualization, H.J. and G.-H.C.; methodology, all authors; software, H.J.; validation, all authors; formal analysis, Y.-Q.L., H.J. and G.-H.C.; investigation, Y.-Q.L., H.J., H.-X.L., S.-J.S., S.-Q.W. and Z.R.; resources, Z.R. and G.-H.C.; data curation, Y.-Q.L.; writing—original draft preparation, Y.-Q.L.; writing—review and editing, G.-H.C.; visualization, Y.-Q.L., H.J. and G.-H.C.; supervision, G.-H.C.; project administration, G.-H.C.; funding acquisition, G.-H.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (12005003), the National Key R&D Program of China (2017YFA0303002), and the Key R&D Program of Zhejiang Province, China (2021C01002).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Wu, W.; Cheng, J.; Matsubayashi, K.; Kong, P.; Lin, F.; Jin, C.; Wang, N.; Uwatoko, Y.; Luo, J. Superconductivity in the vicinity of antiferromagnetic order in CrAs. *Nat. Commun.* **2014**, *5*, 5508. [\[CrossRef\]](#)
- Kotegawa, H.; Nakahara, S.; Tou, H.; Sugawara, H. Superconductivity of 2.2 K under Pressure in Helimagnet CrAs. *J. Phys. Soc. Jpn.* **2014**, *83*, 093702. [\[CrossRef\]](#)
- Bao, J.K.; Liu, J.Y.; Ma, C.W.; Meng, Z.H.; Tang, Z.T.; Sun, Y.L.; Zhai, H.F.; Jiang, H.; Bai, H.; Feng, C.M.; et al. Superconductivity in Quasi-One-Dimensional K₂Cr₃As₃ with Significant Electron Correlations. *Phys. Rev. X* **2015**, *5*, 011013. [\[CrossRef\]](#)
- Tang, Z.T.; Bao, J.K.; Liu, Y.; Sun, Y.L.; Ablimit, A.; Zhai, H.F.; Jiang, H.; Feng, C.M.; Xu, Z.A.; Cao, G.H. Unconventional superconductivity in quasi-one-dimensional Rb₂Cr₃As₃. *Phys. Rev. B* **2015**, *91*, 020506. [\[CrossRef\]](#)
- Tang, Z.T.; Bao, J.K.; Wang, Z.; Bai, H.; Jiang, H.; Liu, Y.; Zhai, H.F.; Feng, C.M.; Xu, Z.A.; Cao, G.H. Superconductivity in quasi-one-dimensional Cs₂Cr₃As₃ with large interchain distance. *Sci. China Mater.* **2015**, *58*, 16–20. [\[CrossRef\]](#)
- Edelmann, M.; Sangiovanni, G.; Capone, M.; de' Medici, L. Chromium analogs of iron-based superconductors. *Phys. Rev. B* **2017**, *95*, 205118. [\[CrossRef\]](#)
- Wang, W.S.; Gao, M.; Yang, Y.; Xiang, Y.Y.; Wang, Q.H. Possible superconductivity in the electron-doped chromium pnictide LaOCrAs. *Phys. Rev. B* **2017**, *95*, 144507. [\[CrossRef\]](#)
- Pizarro, J.M.; Calderón, M.J.; Liu, J.; Muñoz, M.C.; Bascones, E. Strong correlations and the search for high-*T_c* superconductivity in chromium pnictides and chalcogenides. *Phys. Rev. B* **2017**, *95*, 075115. [\[CrossRef\]](#)
- Filsinger, K.A.; Schnelle, W.; Adler, P.; Fecher, G.H.; Reehuis, M.; Hoser, A.; Hoffmann, J.U.; Werner, P.; Greenblatt, M.; Felser, C. Antiferromagnetic structure and electronic properties of BaCr₂As₂ and BaCrFeAs₂. *Phys. Rev. B* **2017**, *95*, 184414. [\[CrossRef\]](#)
- Richard, P.; van Roekeghem, A.; Lv, B.Q.; Qian, T.; Kim, T.K.; Hoesch, M.; Hu, J.P.; Sefat, A.S.; Biermann, S.; Ding, H. Is BaCr₂As₂ symmetrical to BaFe₂As₂ with respect to half 3d shell filling? *Phys. Rev. B* **2017**, *95*, 184516. [\[CrossRef\]](#)
- Das, P.; Sangeetha, N.S.; Lindemann, G.R.; Heitmann, T.W.; Kreyssig, A.; Goldman, A.I.; McQueeney, R.J.; Johnston, D.C.; Vaknin, D. Itinerant G-type antiferromagnetic order in SrCr₂As₂. *Phys. Rev. B* **2017**, *96*, 014411. [\[CrossRef\]](#)
- Mu, Q.G.; Ruan, B.B.; Pan, B.J.; Liu, T.; Yu, J.; Zhao, K.; Chen, G.F.; Ren, Z.A. Superconductivity at 5 K in quasi-one-dimensional Cr-based KCr₃As₃ single crystals. *Phys. Rev. B* **2017**, *96*, 140504. [\[CrossRef\]](#)
- Mu, Q.G.; Ruan, B.B.; Pan, B.J.; Liu, T.; Yu, J.; Zhao, K.; Chen, G.F.; Ren, Z.A. Ion-exchange synthesis and superconductivity at 8.6 K of Na₂Cr₃As₃ with quasi-one-dimensional crystal structure. *Phys. Rev. Mater.* **2018**, *2*, 034803. [\[CrossRef\]](#)
- Wu, W.; Liu, K.; Li, Y.; Yu, Z.; Wu, D.; Shao, Y.; Na, S.; Li, G.; Huang, R.; Xiang, T.; et al. Superconductivity in chromium nitrides Pr₃Cr_{10-x}N₁₁ with strong electron correlations. *Natl. Sci. Rev.* **2019**, *7*, 21–26. [\[CrossRef\]](#)
- Cai, W.; Sun, H.; Xia, W.; Wu, C.; Liu, Y.; Liu, H.; Gong, Y.; Yao, D.X.; Guo, Y.; Wang, M. Pressure-induced superconductivity and structural transition in ferromagnetic CrSiTe₃. *Phys. Rev. B* **2020**, *102*, 144525. [\[CrossRef\]](#)
- Duan, L.; Wang, X.; Zhan, F.; Zhang, J.; Hu, Z.; Zhao, J.; Li, W.; Cao, L.; Deng, Z.; Yu, R.; et al. High-pressure synthesis, crystal structure and physical properties of a new Cr-based arsenide La₃CrAs₅. *Sci. China Mater.* **2020**, *63*, 1750–1758. [\[CrossRef\]](#)
- Pfisterer, M.; Nagorsen, G. Zur struktur ternärer übergangsmetallarsenide/on the structure of ternary arsenides. *Z. Naturforschung B* **1980**, *35*, 703–704. [\[CrossRef\]](#)

18. Singh, D.J.; Sefat, A.S.; McGuire, M.A.; Sales, B.C.; Mandrus, D.; VanBebber, L.H.; Keppens, V. Itinerant antiferromagnetism in BaCr_2As_2 : Experimental characterization and electronic structure calculations. *Phys. Rev. B* **2009**, *79*, 094429. [\[CrossRef\]](#)
19. Paramanik, U.B.; Prasad, R.; Geibel, C.; Hossain, Z. Itinerant and local-moment magnetism in EuCr_2As_2 single crystals. *Phys. Rev. B* **2014**, *89*, 144423. [\[CrossRef\]](#)
20. Park, S.W.; Mizoguchi, H.; Kodama, K.; Shamoto, S.I.; Otomo, T.; Matsuishi, S.; Kamiya, T.; Hosono, H. Magnetic Structure and Electromagnetic Properties of LnCrAsO with a ZrCuSiAs -type Structure ($\text{Ln} = \text{La, Ce, Pr, and Nd}$). *Inorg. Chem.* **2013**, *52*, 13363–13368. [\[CrossRef\]](#)
21. Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. Iron-Based Layered Superconductor $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ ($x = 0.05\text{--}0.12$) with $T_c = 26\text{ K}$. *J. Am. Chem. Soc.* **2008**, *130*, 3296. [\[CrossRef\]](#)
22. Scalapino, D.J. A common thread: The pairing interaction for unconventional superconductors. *Rev. Mod. Phys.* **2012**, *84*, 1383–1417. [\[CrossRef\]](#)
23. Jiang, H.; Bao, J.K.; Zhai, H.F.; Tang, Z.T.; Sun, Y.L.; Liu, Y.; Wang, Z.C.; Bai, H.; Xu, Z.A.; Cao, G.H. Physical properties and electronic structure of $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$ containing CrO_2 and Cr_2As_2 square-planar lattices. *Phys. Rev. B* **2015**, *92*, 205107. [\[CrossRef\]](#)
24. Ablimit, A.; Sun, Y.L.; Jiang, H.; Bao, J.K.; Zhai, H.F.; Tang, Z.T.; Liu, Y.; Wang, Z.C.; Feng, C.M.; Cao, G.H. Synthesis, crystal structure and physical properties of a new oxypnictide $\text{Ba}_2\text{Ti}_2\text{Cr}_2\text{As}_4\text{O}$ containing $[\text{Ti}_2\text{As}_2\text{O}]^{2-}$ and $[\text{Cr}_2\text{As}_2]^{2-}$ layers. *J. Alloys Compd.* **2017**, *694*, 1149–1153. [\[CrossRef\]](#)
25. Xu, X.; Jones, M.A.; Cassidy, S.J.; Manuel, P.; Orlandi, F.; Batuk, M.; Hadermann, J.; Clarke, S.J. Magnetic Ordering in the Layered Cr(II) Oxide Arsenides $\text{Sr}_2\text{CrO}_2\text{Cr}_2\text{As}_2$ and $\text{Ba}_2\text{CrO}_2\text{Cr}_2\text{As}_2$. *Inorg. Chem.* **2020**, *59*, 15898–15912. [\[CrossRef\]](#)
26. Naik, S.P.K.; Iwasa, Y.; Kuramochi, K.; Ichihara, Y.; Kishio, K.; Hongo, K.; Maezono, R.; Nishio, T.; Ogino, H. Synthesis, Electronic Structure, and Physical Properties of Layered Oxypnictides $\text{Sr}_2\text{ScCrAsO}_3$ and $\text{Ba}_3\text{Sc}_2\text{Cr}_2\text{As}_2\text{O}_5$. *Inorg. Chem.* **2021**, *60*, 1930–1936. [\[CrossRef\]](#)
27. Jiang, H.; Sun, Y.L.; Xu, Z.A.; Cao, G.H. Crystal chemistry and structural design of iron-based superconductors. *Chin. Phys. B* **2013**, *22*, 087410. [\[CrossRef\]](#)
28. Liu, J.; Wang, J.; Sheng, J.; Ye, F.; Taddei, K.M.; Fernandez-Baca, J.A.; Luo, W.; Sun, G.A.; Wang, Z.C.; Jiang, H.; et al. Neutron diffraction study on magnetic structures and transitions in $\text{Sr}_2\text{Cr}_3\text{As}_2\text{O}_2$. *Phys. Rev. B* **2018**, *98*, 134416. [\[CrossRef\]](#)
29. Nandi, S.; Xiao, Y.; Qureshi, N.; Paramanik, U.B.; Jin, W.T.; Su, Y.; Ouladdiaf, B.; Hossain, Z.; Brückel, T. Magnetic structures of the Eu and Cr moments in EuCr_2As_2 : Neutron diffraction study. *Phys. Rev. B* **2016**, *94*, 094411. [\[CrossRef\]](#)
30. Tegel, M.; Hummel, F.; Lackner, S.; Schellenberg, I.; Poettgen, R.; Johrendt, D. The Layered Iron Arsenide Oxides $\text{Sr}_2\text{CrO}_3\text{FeAs}$ and $\text{Ba}_2\text{ScO}_3\text{FeAs}$. *Z. Anorg. Und Allg. Chem.* **2009**, *635*, 2242–2248. [\[CrossRef\]](#)
31. Ogino, H.; Katsura, Y.; Horii, S.; Kishio, K.; Shimoyama, J.I. New iron-based arsenide oxides $(\text{Fe}_2\text{As}_2)(\text{Sr}_4\text{M}_2\text{O}_6)(\text{M} = \text{Sc, Cr})$. *Supercond. Sci. Technol.* **2009**, *22*, 085001. [\[CrossRef\]](#)
32. Zhu, W.; Hor, P. $\text{Sr}_2\text{CuGaO}_3\text{S}$, a Rare Example of Square Pyramidal Gallium. *Inorg. Chem.* **1997**, *36*, 3576–3577. [\[CrossRef\]](#)
33. Rodríguez-Carvajal, J. Recent advances in magnetic structure determination by neutron powder diffraction. *Phys. B Condens. Matter* **1993**, *192*, 55–69. [\[CrossRef\]](#)
34. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. [\[CrossRef\]](#)
35. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169–11186. [\[CrossRef\]](#)
36. Wang, Z.; Wu, S.; Ji, L.; Cao, G. Block-layer model for intergrowth structures. *Nano Res.* **2021**, *14*, 3629–3635. [\[CrossRef\]](#)
37. Brown, I.D.; Altermatt, D. Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Crystallogr. Sec. B* **1985**, *41*, 244–247. [\[CrossRef\]](#)
38. White, G.K.; Woods, S. Electrical and thermal resistivity of the transition elements at low temperatures. *Philos. Trans. R. Soc. London. Ser. A Math. Phys. Sci.* **1959**, *251*, 273–302. [\[CrossRef\]](#)
39. Ziman, J.M. *Electrons and Phonons*; Clarendon Press: Oxford, UK, 1960.
40. Mott, N.F. Electrons in transition metals. *Adv. Phys.* **1964**, *13*, 325–422. [\[CrossRef\]](#)
41. Ishikawa, A. Electrical Resistivity Due to Antiferromagnetic Spin Waves in Cr. *J. Phys. Soc. Jpn.* **1982**, *51*, 441–451. [\[CrossRef\]](#)
42. Lumsden, M.D.; Sales, B.C.; Mandrus, D.; Nagler, S.E.; Thompson, J.R. Weak Ferromagnetism and Field-Induced Spin Reorientation in $\text{K}_2\text{V}_3\text{O}_8$. *Phys. Rev. Lett.* **2001**, *86*, 159–162. [\[CrossRef\]](#) [\[PubMed\]](#)
43. McGuire, M.A.; Garlea, V.O.; Kc, S.; Cooper, V.R.; Yan, J.; Cao, H.; Sales, B.C. Antiferromagnetism in the van der Waals layered spin-lozenge semiconductor CrTe_3 . *Phys. Rev. B* **2017**, *95*, 144421. [\[CrossRef\]](#)
44. Clement, R.; Girerd, J.; Morgenstern-Badarau, I. Dramatic modification of the magnetic properties of lamellar manganese trithiophosphonite MnPS_3 upon intercalation. *Inorg. Chem.* **1980**, *19*, 2852–2854. [\[CrossRef\]](#)
45. Chen, H.; McClain, R.; He, J.; Zhang, C.; Olding, J.N.; Dos Reis, R.; Bao, J.K.; Hadar, I.; Spanopoulos, I.; Malliakas, C.D.; et al. Antiferromagnetic Semiconductor $\text{BaFMn}_{0.5}\text{Te}$ with Unique Mn Ordering and Red Photoluminescence. *J. Am. Chem. Soc.* **2019**, *141*, 17421–17430. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Zhu, W.; Hor, P. Crystal Structure of New Layered Oxysulfides: $\text{Sr}_3\text{Cu}_2\text{Fe}_2\text{O}_5\text{S}_2$ and $\text{Sr}_2\text{CuMO}_3\text{S}$ ($\text{M} = \text{Cr, Fe, In}$). *J. Solid State Chem.* **1997**, *134*, 128–131. [\[CrossRef\]](#)
47. de Gennes, P.G. Effects of Double Exchange in Magnetic Crystals. *Phys. Rev.* **1960**, *118*, 141–154. [\[CrossRef\]](#)

-
48. Jeanneau, J.; Toulemonde, P.; Remenyi, G.; Sulpice, A.; Colin, C.; Nassif, V.; Suard, E.; Salas Colera, E.; Castro, G.R.; Gay, F.; et al. Singlet Orbital Ordering in Bilayer $\text{Sr}_3\text{Cr}_2\text{O}_7$. *Phys. Rev. Lett.* **2017**, *118*, 207207. [[CrossRef](#)]