Non-stoichiometry and the magnetic structure of Sr$_2$CrO$_3$FeAs

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Abstract – The iron arsenide Sr$_2$CrO$_3$FeAs with the tetragonal Sr$_2$GaO$_3$CuS-type structure was synthesized and its crystal structure re-determined by neutron powder diffraction. In contrast to previous X-ray crystallographic studies, a mixed occupancy of chromium and iron was found within the FeAs$_4$/4 layer (93 ± 1%Fe:7 ± 1%Cr). We suggest that the partial Cr-doping at the Fe site is the reason for the absence of a spin-density-wave anomaly and superconductivity in this compound. Additional experiments via neutron polarization analysis revealed short-range spin correlations below ∼100 K and long-range antiferromagnetic ordering below $T_N$ = 36 K with a magnetic propagation vector of $q = (\frac{1}{2}, \frac{1}{2}, 0)$. The Cr$^{3+}$-ions form a collinear magnetic structure of the C-type in the magnetic space group $C_{mma}'$ ($a' = a - b, b' = a + b, c' = c$), where Cr$^{3+}$-ions occupy the 4g $(0, \frac{1}{4}, z)$ Wyckoff position. The magnetic moments are aligned along the orthorhombic $a'$-axis. At 3.5 K, an ordered magnetic moment of 2.75 ± 0.05 µ$_B$ for the Cr$^{3+}$ sublattice was refined.

This paper is dedicated to Dr Klaus Römer on the occasion of his 70th birthday.

Introduction. – Since the discovery of superconductivity in tetragonal layered iron arsenides with ZrCuSiAs-, ThCr$_2$Si$_2$-, or PbFCI-type structures [1–3] and critical temperatures up to 55 K [4,5], immense progresses have been made regarding the rich physical and structural phenomena occurring in this new class of superconductors [6,7]. But beyond great efforts to understand the underlying physics, also the search for new compounds with like FeAs layers is important in order to widen the material basis and maybe to increase the critical temperatures.

The $T_c$’s of the so far known iron arsenides increase with the anisotropy of the crystal structures, which is rather small [8] when compared with the cuprates, whose $T_c$’s are also larger. Even though we should be very careful in transferring principles from the cuprates, FeAs-compounds with larger inter-layer distances are of particular interest and recently a number of new compounds with structures derived from copper sulﬁdes with perowskite-like blocks were synthesized and studied. The first was Sr$_3$Sc$_2$O$_3$Fe$_2$As$_2$ [9] with the known structure of Sr$_2$FeO$_3$Cu$_2$S$_2$ [10]. The iron arsenide is not superconducting and shows neither a structural anomaly nor magnetic ordering as found in the ZrCuSiAs and ThCr$_2$Si$_2$-type parent compounds [11,12]. Superconductivity at 17 K has been discovered in the iron phosphide Sr$_2$ScO$_3$FeP [13] with the Sr$_2$GaO$_3$CuS-type structure [14]. This $T_c$ is considerably higher in comparison with the ZrCuSiAs-Type phosphide oxides like LaFePO (4–7 K) and may promise even higher values in analogue arsenides. Indeed, the arsenide Sr$_2$VO$_3$FeAs with $T_c = 37$ K was found [15] and proved the potential of suchlike compounds. The isotypic chromium compound Sr$_2$CrO$_3$FeAs [16,17] is not superconducting,
but exhibits antiferromagnetic order of the Cr$^{3+}$ moments according to susceptibility measurements, whereas $^{57}$Fe-Mössbauer spectra revealed non-magnetic iron atoms in Sr$_2$CrO$_3$FeAs [17,18].

The synthesis of single phase samples of the “21311”-compounds has turned out to be difficult and most of the published X-ray powder patterns reveal significant amounts of impurity phases. This is especially true in the case of the superconducting compound Sr$_2$VO$_3$FeAs and very pronounced in the recently reported Sr$_2$(Mg,Ti)O$_3$FeAs ($T_c = 39$ K) [19], which is hardly the main phase of the sample. Such multi-phase samples cast serious doubts about the true chemical composition of the superconducting fractions.

We have synthesized almost single phase samples of the chromium 21311-compound Sr$_2$CrO$_3$FeAs, which allow a more precise determination of the structure. By neutron scattering we are able to distinguish chromium and iron very well in contrast to X-ray diffraction. In this letter we report the re-determination of the crystal structure and the antiferromagnetic spin structure of Sr$_2$CrO$_3$FeAs. Our results shed light on the absence of superconductivity in Sr$_2$CrO$_3$FeAs and the chemical nature of the 21311-type compounds containing similar d-metals in general.

Experimental methods. – Sr$_2$CrO$_3$FeAs was synthesized by heating stoichiometric mixtures of strontium, chromium, iron oxide and arsenic oxide in alumina crucibles sealed in silica ampoules under an atmosphere of purified argon in four separate batches of 1 gram. Each mixture was heated to 1173 K at a rate of 80 K/h, kept at this temperature for 60 h and cooled down to room temperature. The products were homogenized in an agate mortar, pressed into pellets and sintered at 1323 K for 60 h. The batches were then united, reground, pressed into pellets of 14 mm in diameter and sintered together at 1323 K for 50 h. The obtained black crystalline product Sr$_2$CrO$_3$FeAs is stable in air.

Powder diffraction patterns at various temperatures were recorded at the high flux powder diffractometer D20 at Institut Laue-Langevin (Grenoble, France) with 0.187 nm incident wavelength. Rietveld refinements of the D20 nuclear and magnetic scattering we are able to distinguish chromium and iron very well in contrast to X-ray diffraction. In this letter we report the re-determination of the crystal structure and the antiferromagnetic spin structure of Sr$_2$CrO$_3$FeAs. Our results shed light on the absence of superconductivity in Sr$_2$CrO$_3$FeAs and the chemical nature of the 21311-type compounds containing similar d-metals in general.

Results and discussion. – Figure 1 shows the neutron powder pattern of Sr$_2$CrO$_3$FeAs measured at the D20 diffractometer. It could be fitted successfully with a tetragonal Sr$_2$GaO$_2$CuS-type Sr$_2$CrO$_3$FeAs main phase and FeAs, as well as SrO as minor impurity phases. Yet another small impurity phase could not be identified and
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Fig. 2: (Color online) Crystal structure of Sr$_2$CrO$_3$FeAs. Space group: $P_{\frac{4}{m}}mm$, origin choice 1.

Its largest peak was therefore excluded from the refinement. The crystal structure of Sr$_2$Cr$_2$O$_3$FeAs is shown in fig. 2. No structural phase transition was observed down to 6.5 K. The crystallographic data at 300 K (table 1) are in good agreement with our previously published X-ray data [17]. However, the refinement of the neutron data unambiguously shows a mixed occupancy of iron and chromium at the iron site 2a ($93 \pm 1\% Fe: 7 \pm 1\% Cr$), while no mixed occupancy at the chromium site or any oxygen deficiency were detected within one standard deviation. Full occupancy of all sites was found in X-ray diffraction experiments. These findings suggest partial interchangeability of the 3$d$-metals Fe and Cr in the FeAs layers. This Cr-doping of the Fe-site could explain why Sr$_2$CrO$_3$FeAs does neither display a spin-density-wave (SDW) anomaly nor superconductivity. The situation is very similar to that in Cr-doped BaFe$_2$As$_2$, where small amounts of chromium at the iron site in BaFe$_2$−$_x$Cr$_x$As$_2$ strongly effects the SDW anomaly and it is apparently detrimental to superconductivity [24].

Such mixing of iron with other $d$-metals in the FeAs layers may also occur in other 21331 or 32522-systems, and we do not rule out that the alleged stoichiometric 37 K superconductor Sr$_2$VO$_3$FeAs [15] is in fact a doped compound likewise. Our data do not show any oxygen deficiencies, unlike Sr$_2$VO$_{3-\delta}$FeAs, which was recently reported [25]. However, no detailed structural data of these compounds were published.

| Temperature (K) | 300 |
| Space group     | $P_{\frac{4}{m}}mm$ (01) |
| $a$ (pm)        | 391.71(7) |
| $b$ (pm)        | $a$ |
| $c$ (pm)        | 1578.0(2) |
| $V$ (nm$^3$)    | 0.2421(1) |
| $Z$             | 2 |

Data points: 1446
Excluded regions ($^\circ$ 2$\theta$): 54.9–55.1, 73.9–75.7
Reflections (main phase): 118 (1 excluded)
Profile variables (main phase): 6
Anisotropy variables: 24
Atomic variables (main phase): 15
Background variables: 12
Variables of impurity phases: 21
Other variables: 6
$d$ range: 0.966–15.780
$R_P$, $wR_P$: 0.0304, 0.0452
$R_{bragg}$: 0.0110
$wg$ht. Durbin-Watson $d$ stat.: 0.812

Table 1: Crystallographic data of Sr$_2$CrO$_3$FeAs (D20).

| Atomic parameters: |
|--------------------|
| Sr1                |
| z = 0.8059(3)     |
| $U_{iso} = 131(9)$ |
| Sr2                |
| z = 0.5856(3)     |
| $U_{iso} = 145(12)$ |
| Cr/Fe - occ. 0.99(1):0.01(1) |
| z = 0.3104(4)     |
| $U_{iso} = 69(19)$ |
| Fe/Cr - occ. 0.93(1):0.07(1) |
| z = 0.0883(2)     |
| $U_{iso} = 192(13)$ |
| As                 |
| z = 0.2943(2)     |
| $U_{iso} = 93(7)$ |
| O1                 |
| z = 0.4308(3)     |
| $U_{iso} = 172(12)$ |
| O2                 |
| z = 0.2943(2)     |
| $U_{iso} = 93(7)$ |

Sel. bond lengths (pm): Sr−O 244.3(6) × 1; 251.7(3) × 4 272.6(4) × 4; 278.2(1) × 4 190.0(8) × 1; 197.5(1) × 4 Fe−Fe 277.0(1) × 4 Fe−As 240.4(3) × 4
Sel. bond angles (°): As−Fe−As 109.6(1) × 1; 109.1(2) × 2 O−Cr−O 89.0(1) × 1; 97.4(2) × 4 165.2(4) × 2
Recently reported susceptibility measurements on Sr$_2$CrO$_3$FeAs [17] revealed Curie-Weiss behavior above 150 K with an effective magnetic moment $\mu_{\text{eff}}^{\text{exp}} = 3.83(3) \mu_B$. As this is typical for Cr$^{3+}$-ions in the $^4F_{3/2}$ state ($\mu_{\text{calc}}^{\text{eff}} = 3.87 \mu_B$), we expected that the observed magnetism comes from the chromium atoms only, whereas the iron sites carry no magnetic moments. Furthermore, a drop of the $\chi(T)$ plot below 31 K together with a large negative Weiss constant $\theta = -141(3) \text{K}$ indicated antiferromagnetic ordering. Neutron patterns measured at the D20 diffractometer showed additional peaks appearing below 35 K (not shown). These magnetic reflections could be indexed with the primitive tetragonal cell $|a'| = |a - b| = \sqrt{2} |a|$, $|c'| = |c|$ according to a magnetic propagation vector $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0)$ based on the original tetragonal unit cell. In order to separate nuclear and magnetic scattering, we performed experiments with polarized neutrons at DNS. Sharp magnetic reflections are discernible below $T_N$, indicating long-range antiferromagnetic ordering of the Cr-sublattice (fig. 3). Furthermore, magnetic diffuse scattering due to short-range spin correlations can be clearly observed above $T_N$. At temperatures above 120 K, Sr$_2$CrO$_3$FeAs displays Curie-Weiss–like paramagnetic scattering only. Short-range antiferromagnetic spin correlations begin to emerge below $\sim$100 K. The observed asymmetric diffuse scattering profile strongly suggests that the short-range spin correlations are two-dimensional in nature.

From the observed $\mathbf{q}$-vector ($\frac{1}{2}, \frac{1}{2}, 0$) we assumed a checkerboard-like spin arrangement of the $C$-type, which is reversed between the adjacent chromium layers along $c$. Since the layers are at the coordinates $z = \pm 0.31$, no $G$-type pattern is possible. A first expected spin alignment along $c$ did not reproduce the observed data, therefore we developed models with orientations within the $(ab)$-plane. The by far best fit was found with the alignment along $[a - b]$ and reversed along $a$ and $b$ based on the original tetragonal cell. This arrangement required the orthorhombic magnetic space group $C\Gamma mma'$ (Litvin No. 67.15.591) [26], where Cr$^{3+}$ occupies the $4g$ $(0, \frac{1}{2}, z)$ Wyckoff position and the magnetic moments of Cr$^{3+}$ align along the orthorhombic $a'$-axis, building up a checkerboard arrangement in each Cr layer at both heights $z$ and $\bar{z}$ (fig. 4). By testing different magnetic space groups and different spin orientations, any other model for the magnetic ordering in a direct magnetic subgroup derived from the crystallographic space group $C\Gamma mma$ could be unambiguously ruled out. Sections of the nuclear and magnetic powder patterns recorded at 3.5 K and corresponding Rietveld refinements are depicted in fig. 5. The ordered magnetic moment of a Cr$^{3+}$-ion was refined to be $2.75(5) \mu_B$ at 3.5 K, which is close to the expected $3 \mu_B$. 

Fig. 3: (Color online) Evolution of the magnetic scattering contribution of Sr$_2$CrO$_3$FeAs at different temperatures.

Fig. 4: (Color online) Magnetic ordering of the Cr atoms. Cr atoms at height $z$ are depicted as solid, Cr atoms at height $\bar{z}$ as checkered spheres. The tetragonal crystallographic unit cell is depicted as solid black, the orthorhombic magnetic cell as dashed blue square. The transformation from the tetragonal to the orthorhombic cell is $a' = a - b$, $b' = a + b$, $c' = c$ with an origin shift of $-\frac{1}{2}, \frac{1}{2}, 0$. 

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Fig. 5: (Color online) Magnetic and nuclear reflections of Sr$_2$CrO$_3$FeAs (blue) and Rietveld fit (red) at 3.5 K measured at the polarized spectrometer DNS. The magnetic space group is $C_{P}^{'mm}$ and the crystallographic space group $P_{4}^{1}mmm$. The miller indices of the magnetic reflections were transformed to the tetragonal cell for comparability. Red markers: Reflection conditions of both space groups.

Fig. 6: (Color online) Variation of the refined ordered magnetic moment of the Cr-sublattice with temperature. The temperature dependence follows the simple power law $a \times (T_N - T)^{\beta}$ (red curve).

The evolution of the magnetic ordering becomes evident from the order parameter and its temperature dependence as depicted in fig. 6. It follows the power law $a \times (T_N - T)^{\beta}$ with $a = 2.84(3)$, $T_N = 36.0(5)$ K and $\beta = 0.22(2)$. The exponent $\beta$ is between the idealized 2D and 3D Ising values ($\frac{1}{8}$ and $\frac{5}{16}$, respectively), which agrees with the fact that the magnetic arrangement of each Cr-layer at height $z$ is coupled with the corresponding $\pi$-layer and the magnetism therefore can be explained neither strictly two- nor three-dimensionally.

**Conclusion.** We have synthesized the iron arsenide oxide Sr$_2$CrO$_3$FeAs and re-determined its crystallographic and magnetic structure by neutron diffraction experiments on the D20 and DNS diffractometers. A mixed occupancy of chromium and iron in the FeAs layers was found, which points out the ability of substitution between similar 3d-metals in these compounds. We suggest that this Cr-doping may also be the reason for the absence of a SDW anomaly and superconductivity. Such non-stoichiometries may also occur in similar compounds like the superconducting Sr$_2$VO$_3$FeAs and may also be responsible for the different physical behavior of these compounds when compared with the 1111- and 122-iron arsenides. Deviations from the ideal stoichiometry has especially to be taken into account when discussing their electronic structures. Sr$_2$CrO$_3$FeAs shows short-range spin correlations from the Cr$^{3+}$-ions below $\sim 100$ K and long-range antiferromagnetic ordering below $T_N = 36.0(5)$ K. The magnetic structure is of the C-type with the Cr-spins oriented parallel to [a−b] with all nearest-neighbor Cr$^{3+}$ moments antiferromagnetically aligned, thus forming a checkerboard arrangement.

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