



## Article

# Single Crystal Growth and Anisotropic Magnetic Properties of $\text{Li}_2\text{Sr}[\text{Li}_{1-x}\text{Fe}_x\text{N}]_2$

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**Abstract:** Up to now, investigation of physical properties of ternary and higher nitridometalates has been severely hampered by challenges concerning phase purity and crystal size. Employing a modified lithium flux technique, we are now able to prepare sufficiently large single crystals of the highly air and moisture sensitive nitridoferrate  $\text{Li}_2\text{Sr}[\text{Li}_{1-x}\text{Fe}_x\text{N}]_2$  for anisotropic magnetization measurements. The magnetic properties are most remarkable: large anisotropy and coercivity fields of 7 Tesla at  $T = 2\text{ K}$  indicate a significant orbital contribution to the magnetic moment of iron. Altogether, the novel growth method opens a route towards interesting phases in the comparatively recent research field of nitridometalates and should be applicable to various other materials.

**Keywords:** solution growth; magnetically hard materials; unquenched orbital moment; single crystal; flux growth

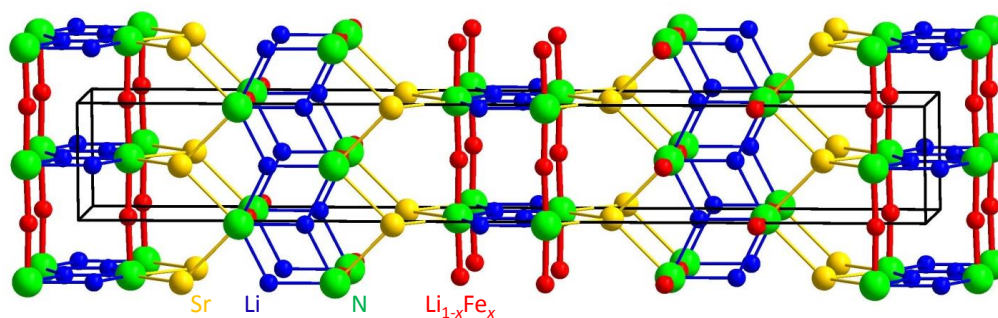
## 1. Introduction

Binary transition metal nitrides attract considerable interest due to their valuable mechanical, electrical and magnetic properties. In contrast, chemistry and physics of multinary nitrides have been far less thoroughly explored [1]. Nitridometalates of  $d$  metals  $T$  represent an interesting class of solid state phases, which contain nitrogen as isolated anions  $\text{N}^{3-}$  or feature complex anions  $[\text{T}_x\text{N}_y]^{z-}$  of different dimensionalities with coordination numbers of  $T$  by  $\text{N}$  typically between two and four and oxidation states of the transition metals being comparatively low. Whereas the bonding within these complex anions and frameworks is essentially covalent, nitridometalates are stabilized by predominantly ionic bonding through counterions of electropositive metals like alkali ( $A$ ) or alkaline-earth ( $AE$ ) cations.

Iron in nitridoferrates of alkali and alkaline-earth metals may be coordinated tetrahedrally ( $\text{Li}_3[\text{Fe}^{\text{III}}\text{N}_{4/2}]$  [2,3]) or trigonal-planar in isolated units ( $(\text{Ca}_3\text{N})_2[\text{Fe}^{\text{III}}\text{N}_3]$  [4],  $\text{Sr}_3[\text{Fe}^{\text{III}}\text{N}_3]$  [5],  $\text{Ba}_3[\text{Fe}^{\text{III}}\text{N}_3]$  [6],  $(\text{Sr}_{1-x}\text{Ba}_x)_3[\text{Fe}^{\text{III}}\text{N}_3]$  [7],  $\text{Sr}_8[\text{Fe}^{\text{III}}\text{N}_3][\text{Fe}^{\text{II}}\text{N}_2]$  [8,9]) as well as in oligomers ( $\text{Ca}_2[\text{Fe}^{\text{II}}\text{N}_2]$  [10],  $\text{Sr}_2[\text{Fe}^{\text{II}}\text{N}_2]$  [10]) and 1D chains ( $\text{LiSr}_2[\text{Fe}^{\text{II}}\text{N}_3]$  [11],  $\text{LiBa}_2[\text{Fe}^{\text{II}}\text{N}_3]$  [11]). Linear coordination is observed as linear dumbbells in  $\text{Sr}_8[\text{Fe}^{\text{III}}\text{N}_3][\text{Fe}^{\text{II}}\text{N}_2]$  [8,9],  $\text{Sr}_8[\text{Mn}^{\text{III}}\text{N}_3][\text{Fe}^{\text{II}}\text{N}_2]$  [12],  $\text{Sr}_2[\text{Fe}^{\text{II}}\text{N}_2]$  [10], and  $\text{Li}_4[\text{Fe}^{\text{II}}\text{N}_2]$  [13], and in linear substituted chains  $[(\text{Li}_{1-x}\text{Fe}_x^{\text{I}})\text{N}]^{2-}$  in  $\text{Li}_2[(\text{Li}_{1-x}\text{Fe}_x^{\text{I}})\text{N}]$  [14–16],  $\text{Li}_2\text{Ca}[(\text{Li}_{1-x}\text{Fe}_x^{\text{I}})\text{N}]_2$  [17],  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x^{\text{I}})\text{N}]_2$  [17],  $\text{LiCa}_2[(\text{Fe}_{1-x}^{\text{I}}\text{Li}_x)\text{N}_2]$  [18] and  $\text{LiSr}_2[(\text{Fe}_{1-x}^{\text{I}}\text{Li}_x)\text{N}_2]$  [19]. Structural data for the majority of nitridoferrates reported up to now were derived from single crystal data, whereas in most cases single phase powder samples had to be employed for the investigation of physical properties, with the exception of  $\text{Li}_2[(\text{Li}_{1-x}\text{Fe}_x^{\text{I}})\text{N}]$  [20] and  $\text{LiSr}_2[(\text{Fe}_{1-x}^{\text{I}}\text{Li}_x)\text{N}_2]$  [19], where single crystals of sufficient size were available for physical properties investigations.

The single crystal growth of nitrides is often challenging due to the large dissociation energy of the  $N_2$  molecule, the reactivity of the starting materials and enhanced vapor pressures. Only recently, Li-rich flux was successfully used for the growth of large single crystals of  $LiCaN$ ,  $Li_3N$  and  $Li_2(Li_{1-x}T_x)N$  with  $T = Mn, Fe, Co$  [20] and  $T = Ni$  [21]. Further development of the high temperature centrifugation aided filtration technique [22–24] by addition of Na and  $NaN_3$  to increase the basicity of the flux also enabled the growth of large single crystals of nitride metalides like  $Li_{16}Sr_6Ge_6N$  [25]. However, the extent of application of this method towards more complex systems, in particular transition metal rich ternary or quaternary nitridometalates that also contain alkaline earth elements, has not been investigated in detail. Magnetic properties were reported only for few nitridometalates containing alkaline-earth metals. Some of these phases show ferromagnetic ( $LiSr_2[CoN_2]$  [19]) or antiferromagnetic ( $LiSr_2[FeN_2]$  [19]) ordering. Furthermore, for many phases (for example  $Sr_8[MnN_3]_2[MnN_2]$  [26]) a large spin-orbit coupling together with low or intermediate spin states is being discussed.

We shall present results on Fe-substituted  $Li_4SrN_2$ . The peculiar (almost) linear, two-fold coordination of Fe makes this material particularly promising since unprecedented magnetic coercivity and anisotropy were found in Fe-substituted  $Li_3N$ , which shares the same structural feature [16,27]. Synthesis and crystal structure of Fe-substituted  $Li_4SrN_2$  was first reported by Klatyk and Kniep [17]: Small single crystals sufficient for X-Ray diffraction were obtained by reaction of Li,  $Li_2(Li_{0.66}Fe_{0.33})N$  and  $Sr_2N$  in a molar ratio of 7:6:4. The compound crystallizes in a tetragonal lattice, space group  $I4_1/amd$  (No. 141) with  $a = 3.7909(2)$  Å, and  $c = 27.719(3)$  Å. As indicated by the notation of the chemical formula,  $Li_2Sr[(Li_{1-x}Fe_x)N]_2$  with  $x = 0.46$ , the substituted Fe atoms occupy only one of the two Li-sites (the one in two-fold coordination of N, see Figure 1). The Fe-coordination is not strictly linear. Rather the N–Fe–N angle amounts to  $177.4^\circ$  as inferred from the reported crystal structure [17]. The Fe-substitution causes a decrease of  $a$  but an increase of  $c$  by 0.8% and 2.5%, respectively, compared to the parent compound  $Li_4SrN_2$  [28]. No physical properties have been reported so far.



**Figure 1.** Crystal structure of  $Li_2Sr[(Li_{1-x}Fe_x)N]_2$ , the unit cell is indicated by the black lines (space group  $I4_1/amd$ ). Fe is substituted in linear, two-fold coordination between N.

Here we show that  $Li_2Sr[(Li_{1-x}Fe_x)N]_2$  single crystals of several millimeter along a side can be obtained from Li-rich flux. The large magnetic anisotropy and coercivity revealed a significant orbital contribution to the magnetic moment of Fe. Cu-substituted  $Li_4SrN_2$  was investigated as a non-local-moment-bearing reference compound.

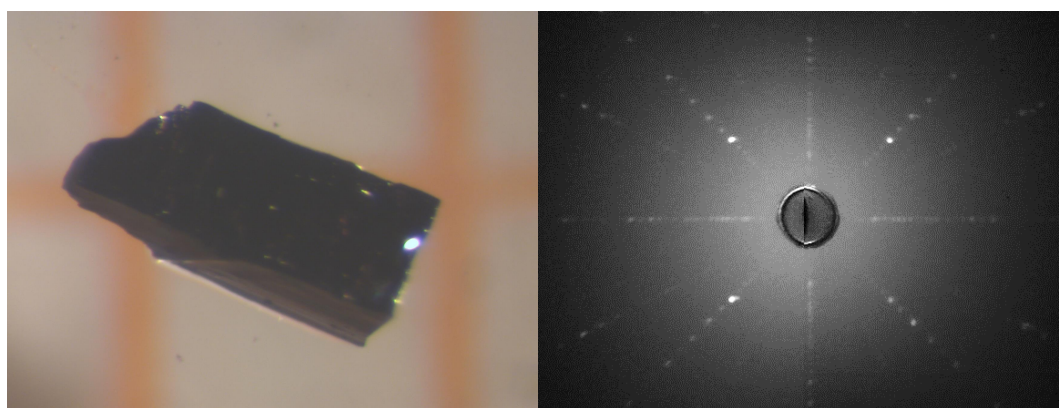
## 2. Results

### 2.1. Single Crystal Growth

Due to the air and moisture sensitivity of both the reactants (Li,  $Sr_2N$ ,  $NaN_3$ ) and the final product  $Li_2Sr[(Li_{1-x}Fe_x)N]_2$  all manipulations including grinding and weighing, as well as complete

sample preparations for measurements were carried out in an inert gas glove box ( $\text{Ar}$ ,  $\text{O}_2$  and  $\text{H}_2\text{O} \leq 1$  ppm). The title compound was obtained in form of large, black single crystals from the reaction of  $\text{Sr}_2\text{N}$ , Fe, Li and  $\text{NaN}_3$  in molar ratio 1:1.8:36:1 with  $\text{NaN}_3$  acting as nitrogen source and Li acting as flux and mineralizer. The mixtures with a total mass of roughly 0.6 g were placed in a tantalum ampule [29]. The whole device was sealed by arc welding under inert atmosphere of 700 mbar argon and subsequently encapsulated in a quartz tube with an internal argon pressure of 300 mbar in order to prevent oxidization of the tantalum. The sample was heated from room temperature to  $T = 700^\circ\text{C}$  within 7 h, annealed for 2 h, then cooled to  $T = 300^\circ\text{C}$  within 400 h, and finally centrifuged with  $3000\text{ min}^{-1}$  to separate the single crystals of a blackish color from the excess flux. Besides several large single crystals of the title phase, small amounts of single crystalline  $\text{Li}_3\text{N}$  and  $\text{LiSr}_2[(\text{Fe}_{1-x}\text{Li}_x)\text{N}_2]$  [19] were also obtained. Using a two-probe multimeter, the different phases showed remarkably different resistivities enabling the discrimination of the various phases.

A representative  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$  single crystal is shown in Figure 2. The samples show a plate-like habit with the crystallographic  $c$ -axis oriented perpendicular to the large surface as confirmed by Laue-back-reflection (right panel in Figure 2). The spot-size of the X-Ray beam was similar to the sample size.



**Figure 2.**  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$  single crystal ( $x = 0.41$ ) on a millimeter grid (**left**) and corresponding Laue-back-reflection pattern to the **right** showing the four-fold rotational symmetry along the crystallographic  $c$ -axis.

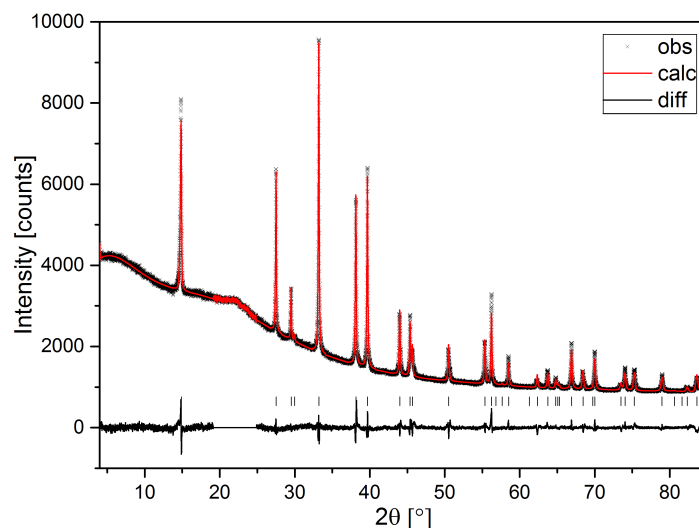
An Fe-concentration of  $x = 0.42$  was determined by energy-dispersive X-Ray analysis (EDX) based on the Fe:Sr ratio and assuming fully occupied Sr-sites. An almost identical value of  $x = 0.41$  was found by chemical analysis by means of inductively coupled plasma optical emission spectroscopy (ICP-OES; accessible is the Li:Sr:Fe ratio) and was confirmed with a second sample taken from the same batch. The observed slight Li-excess of 0.15 per formula unit (0.19 for the other sample), is attributed to small amounts of Li-rich flux remnants.

## 2.2. Crystal Structure

Figure 3 shows the X-Ray powder diffraction pattern measured on ground  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$  single crystals. No foreign phases were detected. The region between  $2\theta = 20^\circ$ – $25^\circ$  was excluded due to amorphous constituents that are created by degradation during the measurement. Lattice parameters of  $a = 3.79536(9)\text{ \AA}$  and  $c = 27.6492(13)\text{ \AA}$  and an Fe occupancy of  $x = 0.32$  were obtained by Rietveld refinement. The decrease in  $a$  and increase in  $c$  in comparison to the parent compound  $\text{Li}_4\text{SrN}_2$  ( $a = 3.822(2)\text{ \AA}$  and  $c = 27.042(9)\text{ \AA}$  [28]) are slightly smaller than reported in Ref. [17] ( $x = 0.46$ ,  $a = 3.7909(2)\text{ \AA}$  and  $c = 27.719(3)\text{ \AA}$ ) in accordance with a somewhat lower Fe concentration.

Smaller crystals were obtained from crushed samples and selected for single crystal X-Ray diffraction. The results are summarized in Table 1. Powder as well as single crystal X-Ray diffraction

revealed an Fe-concentration of  $x = 0.32$ . This is somewhat smaller than the values obtained by EDX and chemical analysis and indicates that the Fe concentration may vary between different samples; the slight difference between powder and single crystal data may also stem from slight inhomogeneities within the samples. The single crystal used for the magnetization measurements (see below) was directly analyzed by ICP-OES and showed an iron concentration of  $x = 0.41$ .



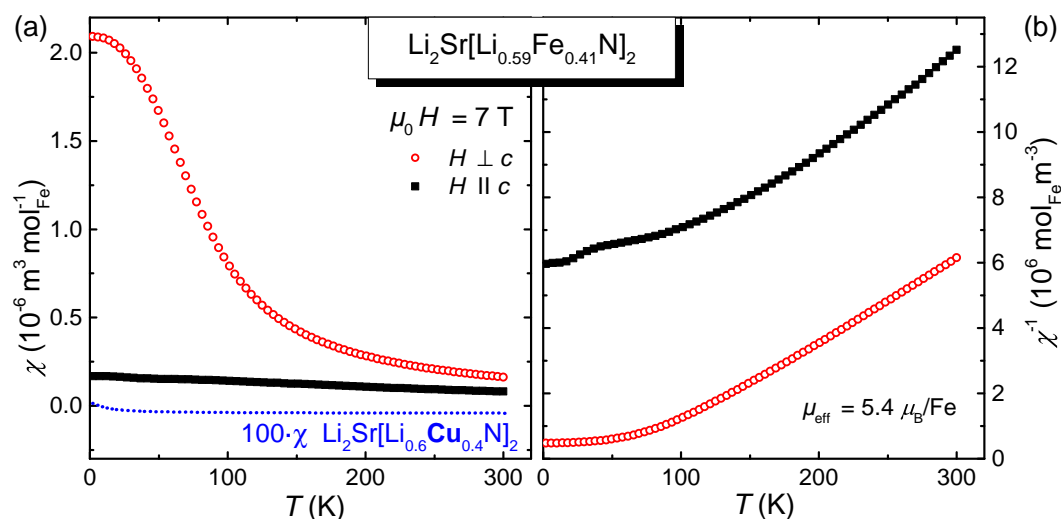
**Figure 3.** X-Ray diffraction pattern measured on ground single crystals of  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$  (Co- $K\alpha$  radiation,  $\lambda = 1.78892 \text{ \AA}$ ). Tick marks correspond to reflection positions of  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$ .

**Table 1.** Single crystal structure refinement for  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$ .

|   |                                |
|---|--------------------------------|
| crystal system  | tetragonal                     |
| space group   | $I4_1/amd$ (No. 141)           |
| $a$ (Å)   | 3.8011(1)                      |
| $c$ (Å)   | 27.586(3)                      |
| Fe occupancy ( $x$ )  | 0.32(1)                        |
| cell volume (Å <sup>3</sup> )   | 398.57(5)                      |
| $Z$   | 4                              |
| $\rho_{\text{calcd}}$ (gcm <sup>−3</sup> )                              | 2.907                          |
| crystal color, habit  | black, tetragonal column       |
| crystal size (mm)   | $0.02 \times 0.02 \times 0.07$ |
| $\mu(\text{MoK}\alpha, \text{mm}^{-1})$                                 | 15.52                          |
| $2\theta$ range (°)   | 5.90–59.60                     |
| diffractometer  | RIGAKU AFC7                    |
| wavelength (Å)  | 0.71069 (Mo- $K\alpha$ )       |
| monochromator   | graphite                       |
| temperature   | 293 K                          |
| scan mode   | profile data from $\phi$ scans |
| measured reflections  | 3355                           |
| observed reflections [ $F_o > 4\sigma(F_o)$ ]                           | 2919                           |
| independent reflections   | 187                            |
| $R_{\text{int}}$  | 0.041                          |
| structure solution method   | direct                         |
| number of parameters  | 17                             |
| goodness-of-fit on $F^2$  | 1.081                          |
| $wR2$   | 0.078                          |
| $R1$ [ $F_o > 4\sigma(F_o)$ ]   | 0.030                          |
| $R1$ (all data)   | 0.035                          |
| residual electron density ( $\text{e} \times 10^{-6} \text{ pm}^{-3}$ ) | 1.24/−1.70                     |

### 2.3. Magnetic Properties

The temperature-dependent magnetic susceptibility  $\chi(T) = M/H$  measured parallel and perpendicular to the crystallographic  $c$ -axis is shown in Figure 4a (field-cooled in  $\mu_0 H = 7$  T). A temperature-independent contribution of a ferromagnetic impurity phase (with a Curie temperature significantly above room temperature, presumably elemental Fe or  $\text{Fe}_3\text{O}_4$ ) was subtracted by assuming that the intrinsic, local-moment contribution of the title compound is linear in field at  $T = 300$  K (analogous to the Honda-Owen method). A pronounced anisotropy is observed over the whole temperature range investigated. The ratio of  $\chi_{\perp c}/\chi_{\parallel c}$  increases upon cooling from a value of 2 at  $T = 300$  K to 12 at  $T = 2$  K.



**Figure 4.** Magnetic susceptibility  $\chi = M/H$  per mol Fe as a function of temperature for field applied parallel and perpendicular to the crystallographic  $c$ -axis. (a) A pronounced anisotropy with larger  $\chi$  for  $H \perp c$  (open, red symbols) is observed up to room temperature. The molar susceptibility of  $\text{Li}_2\text{Sr}[(\text{Li}_{0.6}\text{Cu}_{0.4})\text{N}]_2$  multiplied by a factor of 100 is shown for comparison (blue, dotted line,  $H \perp c$ ); (b) The temperature dependence of the inverse susceptibility roughly follows a Curie-Weiss law for  $T > 150$  K.

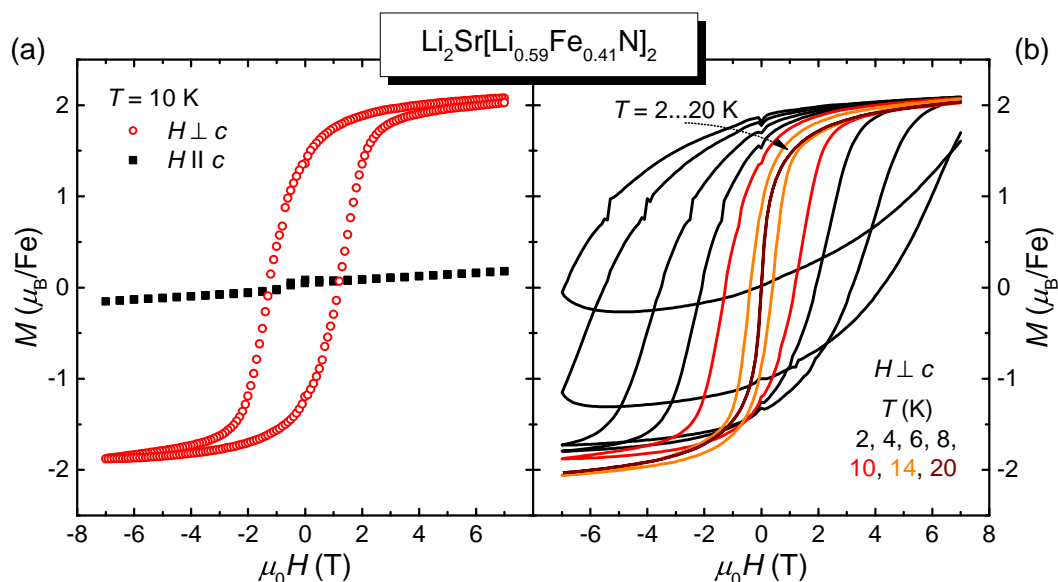
In order to confirm the proposed, unusual valence state of Fe(I) [17], we performed further magnetization measurements on isotypic  $\text{Li}_2\text{Sr}[(\text{Li}_{0.6}\text{Cu}_{0.4})\text{N}]_2$  (the sample was grown similar to the title compound  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$ ). The local moment behavior associated with the spin-1/2 of Cu(II) is supposed to be markedly different from the one of Cu(I). As shown by the blue, dotted line in Figure 4a, the susceptibility of  $\text{Li}_2\text{Sr}[(\text{Li}_{0.6}\text{Cu}_{0.4})\text{N}]_2$  does not show local moment behavior and is indeed negligibly small compared to the one of the Fe-substituted homologue. The largely temperature independent value of  $\chi = -5(1) \times 10^{-10} \text{ m}^3 \cdot \text{mol}^{-1}$  is in reasonable agreement with the ionic diamagnetic contribution of the  $\text{Li}_4\text{SrN}_2$  host material of  $\chi = -6 \times 10^{-10} \text{ m}^3 \cdot \text{mol}^{-1}$  {assuming  $\chi(\text{Li}^{1+}) = -0.09 \times 10^{-10} \text{ m}^3 \cdot \text{mol}^{-1}$  [30],  $\chi(\text{Sr}^{2+}) = -2 \times 10^{-10} \text{ m}^3 \cdot \text{mol}^{-1}$  [31] and  $\chi(\text{N}^{3-}) = -1.6 \times 10^{-10} \text{ m}^3 \cdot \text{mol}^{-1}$  [32]}. Accordingly, the observed non-local moment behavior of  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Cu}_x)\text{N}]_2$  implies the presence of Cu(I) and supports a valence state of Fe(I).

The inverse susceptibility roughly follows a Curie-Weiss law for  $T = 150\text{--}300$  K (Figure 4b). For  $H \perp c$  an effective moment of  $\mu_{\text{eff}} = 5.4 \mu_{\text{B}}$  per Fe and a ferromagnetic Weiss temperature of  $\Theta_{\text{W}} = 49$  K were obtained. The fit to the data considered a minor diamagnetic contribution of  $\chi_0 = -1.5 \times 10^{-8} \text{ m}^3 \cdot \text{mol}^{-1}$  (10% of the absolute value at room temperature). The slope of  $\chi^{-1}$  suggests a similar value of the effective moment for  $H \parallel c$ , however, the small absolute value of  $\chi$  in combination with a large antiferromagnetic Weiss temperature prohibits an accurate estimate.



The isothermal magnetization in  $\mu_B$  per Fe as a function of an applied magnetic field at  $T = 10$  K is shown in Figure 5a. For  $H \parallel c$  the magnetization increases slowly with the applied field in a linear fashion without any appreciable hysteresis. The magnetization is significantly larger for  $H \perp c$  and exceeds values of  $2 \mu_B$  per Fe. However, no saturation is observed even at the largest available field of  $\mu_0 H = 7$  T. In accordance with the large anisotropy, a pronounced hysteresis loop with a coercive field of  $\mu_0 H_c = 1.2$  T forms for  $H \perp c$ . The coercivity field increases rapidly upon cooling (Figure 5b). At the lowest accessible temperature  $T = 2$  K the coercivity reaches almost 7 T. The hysteresis vanishes for temperatures higher than  $T \approx 16$  K. Furthermore, the  $M - H$  loops are asymmetric for  $T < 14$  K: The (field cooled) value in  $\mu_0 H = +7$  T is larger than the corresponding value found at  $\mu_0 H = -7$  T.

The small anomalies at  $H \sim 0$  and at  $M \sim 1 \mu_B$  result from the subtraction of the ferromagnetic impurity contribution (which is not fully temperature independent) and a zero-crossing of the raw data signal, respectively. A significant in-plane anisotropy for different orientations perpendicular to the  $c$ -axis could be present, in particular  $\langle 100 \rangle$  vs.  $\langle 110 \rangle$  (see discussion). The closer investigation of this anisotropy, however, is beyond the scope of this publication.



**Figure 5.** Isothermal magnetization in  $\mu_B$  per Fe at  $T = 10$  K; (a) Large hysteresis emerges for field applied perpendicular to the  $c$ -axis (which is perpendicular to the N–Fe–N ‘molecular axis’); (b) The hysteresis for  $H \perp c$  increases rapidly with decreasing temperature. Spontaneous magnetization disappears for temperatures larger than  $T \sim 16$  K.

### 3. Discussion

The successful use of a Li-rich flux for the growth of large single crystals of Fe-substituted  $\text{Li}_4\text{SrN}_2$  has been anticipated since there are only a few binaries known that may compete with the formation of this compound. Among those, Li–Sr binaries are not considered exceedingly stable as indicated by their low peritectic decomposition temperatures ( $< 200$  °C) [33]. Nevertheless, a good solubility of Sr in Li is inferred. Only a few Sr–N binary compounds are known and none of those seem to be stable in the presence of Li. No binary compounds of Sr–Fe or Sr–Ta (which may prevent the use of Ta crucibles) are known. Furthermore, our work shows that  $\text{Li}_3\text{N}$  is not so stable that it prevents the formation of other nitrides. Whether the related compounds  $\text{LiSr}_2\text{Fe}_2\text{N}_3$  [11] or  $\text{LiSr}_2\text{FeN}_2$  [19] (isotypic to  $\text{LiSr}_2\text{CoN}_2$  [34]) can be grown as large single crystals by adjusting temperature profile and/or ratio of the starting materials is subject of ongoing research. The situation is similar for ternary and multinary nitrides that contain other alkaline earth and/or other transition metals and it seems not unlikely to find a wide range of applications for the Li-flux method.

The magnetic properties of  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$ , in particular the large anisotropy and coercivity, are most remarkably. There are only a few materials known that show coercivity fields in the range of  $\mu_0 H_c \sim 7$  T or above. Those are melt-spun ribbons of rare-earth-based Dy–Fe–B and Tb–Fe–B alloys (reported are  $\mu_0 H_c = 6.4$  T for both materials [35] and  $\mu_0 H_c = 7.7$  T for the latter one [36]). For transition-metal-based compounds, the only examples we are aware of are  $\text{LuFe}_2\text{O}_4$  ( $\mu_0 H_c = 9$  T [37] and  $\mu_0 H_c = 11$  T [38]) and Fe-substituted  $\text{Li}_3\text{N}$  ( $\mu_0 H_c = 11.6$  T [27]). The large magnetic anisotropy and coercivity of both materials is caused by a significant orbital contribution to the magnetic moment of Fe (see [39] for the former and [21,40–42] for the latter one). Whereas the emergence of the orbital moment in  $\text{LuFe}_2\text{O}_4$  is a result of a complex interplay between charge ordering, ferroelectricity and ferrimagnetism [43], the orbital moment in Fe-substituted  $\text{Li}_3\text{N}$  seems to be directly linked to the linear, two-fold coordination of Fe [27]. Such a linear molecule or linear chain is not subject to a Jahn-Teller distortion [44,45] which is the driving force for the quenching of the orbital magnetic moment that is usually observed in transition metals.

As found for Fe-substituted  $\text{Li}_3\text{N}$ , the magnetic hard axis of  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$  is oriented perpendicular to the N–Fe–N “molecular axis” (see Figures 1 and 5). Accordingly, there is no unique easy-axis present in  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$  since the N–Fe–N molecules run along both the *a*- and the *b*-axes (in contrast to Fe-substituted  $\text{Li}_3\text{N}$  where the N–Fe–N molecules do define the easy axis and are oriented along the unique, hexagonal *c*-axis). The magnetization in the *a*–*b* plane is therefore expected to reach between 1/2 and  $1/\sqrt{2}$  of the saturation magnetization of Fe corresponding to field along  $\langle 100 \rangle$  and  $\langle 110 \rangle$ , respectively. The increase of the magnetization for  $H \perp c$  is only slightly larger than for  $H \parallel c$  (see Figure 5a). This implies similar large magnetic anisotropy energies for  $\langle 110 \rangle$  and  $\langle 001 \rangle$  (with respect to  $\langle 100 \rangle$ ).

To summarize, the large magnetic anisotropy and coercivity observed in  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$  give strong evidence for a significant orbital contribution to the magnetic moment of Fe. The similarities to  $\text{Li}_2(\text{Li}_{1-x}\text{Fe}_x)\text{N}$  [21,27] are apparent. The origin of this behavior is attributed to the (almost) linear, two-fold coordination Fe. Our work shows that small deviations from linearity, that is a N–Fe–N angle of  $\sim 177^\circ$  instead of  $180^\circ$ , do not prevent the formation of unquenched orbital moments. This finding significantly increases the number of materials that are promising for the investigation of orbital moment formation in transition metal compounds.

#### 4. Materials and Methods

Starting materials were lithium rod (Evochem, 99%), iron powder (Alfa Aesar 99.998%), strontium nitride ( $\text{Sr}_2\text{N}$ ) powder (prepared from strontium metal (Alfa Aesar, distilled dendritic pieces, 99.8%) and nitrogen (Praxair, 99.999%, additionally purified by molecular sieves)), and sodium azide ( $\text{NaN}_3$ ) powder (Roth, 99%) as a further nitrogen source. Tantalum ampules were produced on-site from pre-cleaned tantalum tube and tantalum sheet in an arc furnace located within a glove box.

Laboratory powder X-ray diffraction data of finely ground (gray) powder samples were collected on a Huber G670 imaging plate Guinier camera using a curved germanium (111) monochromator and  $\text{Cu-K}\alpha_1$  radiation in the range  $4^\circ \leq 2\theta \leq 100^\circ$  with an increment of  $0.005^\circ$  at 293(1) K. The powder samples were placed between Kapton foils to avoid degradation in air. Preliminary data processing was done using the WinXPow program package [46]. Rietveld refinement of the structure of  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$  was performed with the software package Jana2006 [47]. Small intervals of the diffraction pattern between  $2\theta = 20^\circ$ – $25^\circ$  corresponding to amorphous degradation products were excluded during the refinement. After background correction, profile and lattice parameters were refined by using Pseudo-Voigt profile functions and Berar-Baldinozzi’s asymmetry model before refining atomic positions and isotropic thermal displacement factors.

The crystal structure and the composition of the title compound  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$  was refined from single-crystal X-ray diffraction data which were collected at room temperature on a Rigaku AFC7 four circle diffractometer equipped with a Mercury-CCD detector ( $\text{Mo-K}\alpha$

radiation, graphite monochromator). After data collection the structures were solved by direct methods, using SHELXS-97 [48] and subsequently refined by using the full-matrix least-squares procedure with SHELXL-97 [49]. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-432385 (powder) or CSD-432386 (single crystal), the names of the authors, and the journal citation. The morphology of the  $\text{Li}_2\text{Sr}[(\text{Li}_{1-x}\text{Fe}_x)\text{N}]_2$  sample and its metal composition were investigated using a scanning electron microscope Philips XL30 equipped with a Bruker Quantax EDX-System (Silicon drift detector,  $\text{LaB}_6$  cathode). The EDX data were processed using the Esprit-Software. The composition of the samples was further analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian Vista-MPX. To this extent the samples were dissolved in dilute hydrochloric acid solution (4 mL of 37% hydrochloric acid added to 46 mL deionized water). Laue back reflection pattern were taken with a digital Dual FDI NTX camera manufactured by Photonic Science (tungsten anode,  $U = 20$  kV). The magnetization was measured using a 7 T Magnetic Property Measurement System (MPMS3) manufactured by Quantum Design.

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**Author Contributions:** Peter Höhn grew the single crystals and analyzed powder and single crystal X-Ray diffraction data that were collected by Yuri Prots; Tanita J. Ballé performed the magnetization measurements and interpreted the data; Manuel Fix collected and analyzed Laue-back-reflection data; Anton Jesche wrote the paper with the help of all authors.

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

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