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Magnetic and Superconducting Properties of FeAs-based High-Tc Superconductors with Gd

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We report on successful synthesis under high pressure of a series of polycristalline GdFeAs $O_{1-x}F_x$ high-T_c superconductors with different oxigen deficiency $x = 0.12 \div 0.16$ and also with no fluorine. We have found that the high-pressure synthesis technique is crucial for obtaining the single-phase superconducting materials: by sythesizing the same compounds with no pressure in ampoules, we obtained non-superconducting materials with an admixure of incidental phases. Critical temperature for all the materials was in the range 40 to 53 K. The temperature derivative of the critical field dH_{c2}/dT is remarkably high, indicating potentially high value of the second critical field $H_{c2} \sim 130$ T.

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Recent discovery of a new class of high temperature superconductors based on iron [1, 2] came as a big surprise to the theory; it has sparked vast interest and stimulated intensive experimental and theoretical research of the superconductvity in this class of material. The first discovered high temperature pnictide superconductor $LaFeAsO_{1-x}F_x$ had a critical temperature $T_c = 26$ K [1], the substitution of La by Se, Sm, Pr, Nd was shown to increase critical temperature [3]. The highest $T_c \approx 54$ K was found for $SmFeAsO_{1-x}$ with optimized oxigen deficiency $x = 0.2$ [4].

High interest to these compounds is stimulated by the theoretical suggestion that the superconductivity in iron-based superconductors is unconventional and mediated by spin fluctuations [5 – 7] Another point of interest is an unusual combination of magnetic ordering and superconducting pairing in the same material. The existence of the spin density wave ordering in the superconducting phase gives rise to the unusual $s_\pm$ type pairing symmetry [6, 8 – 10]. The structure of the so called 1111-compounds $RZFeAsO_{1-x}F_x$ (RZ=La, Ce, Pr, Nd, Sm, Gd, Tb, Dy) consists of alternating RZO and FeAs layers stacking along the c-axis [11]. Doping of the compounds with $n-$ or $p-$ type carriers is achieved by partial substitution of F with O, or by oxigen deficiency, correspondingly [11, 12].

Due to its high critical temperature (~ 54 K), Sm-based FeAs-superconductor is studied in most detail. In the current paper we focuse on much less studied Gd-based FeAs material. There were reports about $T_c = 36$ K for $GdFeAsO_{0.83}F_{0.17}$ [13]. In this paper we describe method of synthesis of single-phase superconducting polycrystals of this material with various amount of oxigen and fluorine. For optimally doped GdFeAs-based superconductor, we obtained $T_c = 53$ K and estimated $H_{c2} \sim 130$ T.

Synthesis. Two methods for solid state synthesis of polycrystalline pnictides at high temperatures were mentioned in literature [11, 12, 14]: synthesis in evacuated quartz ampoules, and synthesis at high pressure. We tested both methods and found that the reproduceable high quality, single-phase material is obtained only in high pressure synthesis. The starting materials for synthesis were high purity chips of Gd and As (99.9%) and powders FeF_3, Fe, and Fe_2O_3 (99.99%). Initially, the chips of Gd and As were placed in an evacuated quartz ampoule and heated at $T = 1050$°C during 24h. The purity of the synthesized FeAs phase was tested by

the powder X-ray diffraction. The resulting single-phase FeAs powder, FeF_3, Fe, and Fe_2O_3 powders were mixed together with the nominal stoichiometric ratio, and then pressed into pellets (3 mm od and 3mm height).

For high pressure synthesis we used "Conac-28" high pressure apparatus [15]. The pellets were inserted in boron nitride crucible and synthesized at pressure of 50 kb and temperature 1350 °C during 60 min. Further, the temperature was either (i) decreased to 1200 °C in 60 min and then heating was switched off, or switched off right after 60min-stage of synthesis. The X-ray diffraction (XRD) pattern (Fig.1) demonstrates that the resulting substance is practically a pure single-phase polycrystalline material.

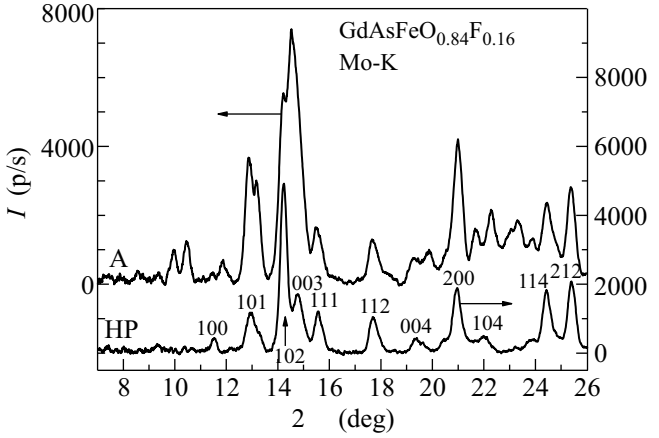

Fig.1. X-ray diffraction pattern for two samples of the nominally same composition and fabricated by ampoule (A) and high pressure (HP) synthesis. Monotonic background is subtracted in both cases. Peaks are indexed according to $P4/nmm$ symmetry of the lattice [12]

For ampoule synthesis the pellets (prepared as described above) were inserted in fused quarts evacuated ampoules and were sintered in oven at temperature 1180 °C during 24 hours. Samples produced by the ampoule synthesis showed similar XRD pattern (see Fig.1), however additional peaks evidence for a noticeable admixture of incidental phases. All samples synthesized in ampoules were non-superconducting. Re-grinding the sintered pellets and repetion of the synthesis in ampoules did not help to produce the desired superconducting phase. However, after the pellets were re-synthesized under high pressure, as described above, the materials became superconducting with XRD pattern and other properties similar to those for the materials synthesized at high pressure directly from powders. We conclude that the ampoule reaction techniqe is not suitable and does not enable to obtain desirable single-phase GdFeAs OF-compound.

X-ray diffraction was taken at room temperature using Mo-K_α radiation. All characteristic peaks in the spectra (Fig.1) are identified and evidence for a single-phase polycristalline material. The XRD pattern in Fig.1 is presented for a typical sample synthesized by the HP technique and, for comparison, for another sample of a nominally similar composition but synthesized by the ampoule technique.

For the single-phase samples synthesized at high pressure, we performed measurements of the magnetic susceptibility (by ac-technique, at $\approx$ 900 Hz, and with modulation amplitude 0.1 Oe) and resistivity (by standard four-probe technique). Figure 2 shows temperature dependence of the susceptibility in zero magnetic field, measured for four samples with various content of oxigen and fluorine. All samples exhibit a sharp superconducting transition with a critical temperature T_c ranging from 35 to 50 K. The critical temperature which is higher than that for some high temperature superconductors, such as MgB_2 (T_c = 39 K) and for $LaBa_{-x}CuO_4$ (T_c = = 36 K), but lower than for $YBa_2Cu_3O_{7-x}$ (T_c = 90 K), is the evidence that the material belongs to the class of high temperature superconductors (HTSC).

For comparison, the insert to Fig.2 shows ac-susceptibility measured for three samples sinthesized in ampoules. Symbols on the main panel and on the insert refer to nominally the same amount of oxigen and fluorine. Clearly, the samples produced by ampoule synthesis are not superconducting, at least above 2 K, and show an antiferromagnetic type dependence with Neel temperature $\Theta_N \approx 17$ K. It is worthnoting that the samples synthesized at high pressure in the normal state ex-

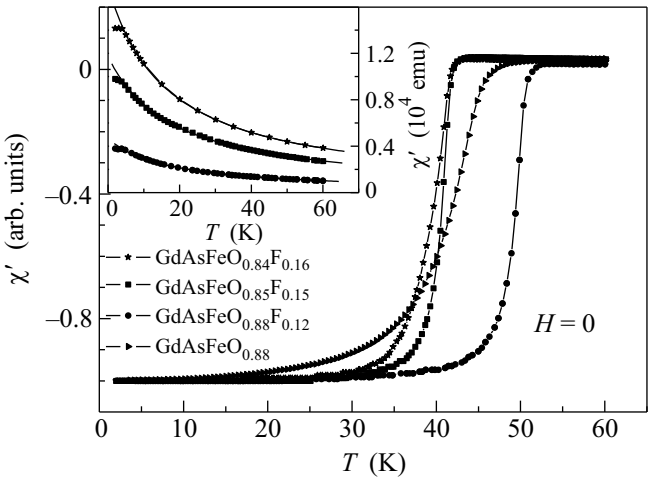

Fig.2. Temperature dependence of the real part of ac-susceptibility measured at zero magnetic field for four samples. The isert shows susceptibility for three samples with nominally the same content, but synthesized in ampoules

hibit a paramagnetic temperature dependence (though almost indistinguishible from antiferromagnetic type dependence in the available temperature range).

As seen from Fig.2, the $GdFeAsO_{0.88}F_{0.12}$ sample has the highest $T_c \approx 50$ K among the four synthesized samples. For this "optimally" (or almost opmilally) doped sample we present in Fig.3 temperature depen-

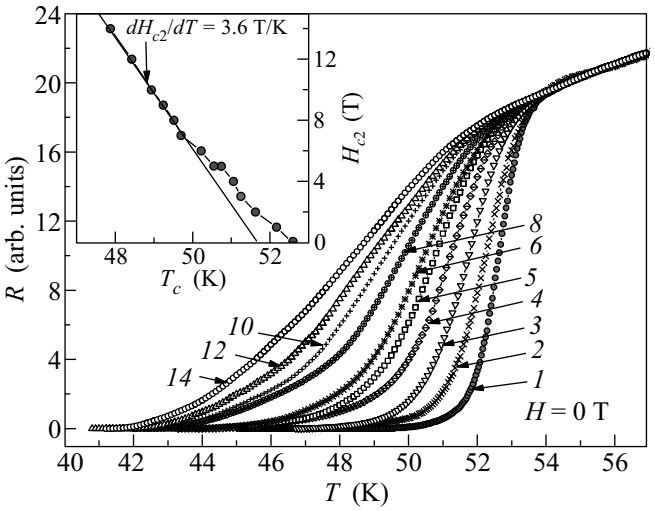

Fig.3. Temperature dependence of the resistance for various magnetic fields. Labels next to curves designate external magnetic field value in Tesla. The insert shows temperature dependence of the critical field H_{c2}, determined from data on the main panel at the middle of the transition

dence of the resistance, measured in various magnetic fields. As magnetic field increases, the critical temperature decreases and the width of the transition increases; as a result, the beginning of the superconducting transition stays almost unchanged. Such behavior is typical for type II superconductors, and particularly, for $SmFeAsO_{0.7}F_{0.29}$ [14]. The critical temperature determined from the temperature dependence of resistance is 52.5 K, noticeably higher than that determined from the $\chi'(T)$ measurements. Such difference is characteristic for type II superconductors.

In order to evaluate relative content of the superconducting phase in the sample, we compare in Fig.4 the temperature dependence of the magnetic susceptibility measured for different conditions:

(a) "Zero field cooling" (ZFC) – the sample was cooled in zero magnetic field, further, the required magnetic field was applied at the lowest temperature (2K) and the ac-susceptibility was measured during warming the sample in the given field.

(b) "Field cooling" (FC) – the required magnetic field was applied at a temperature much higher than T_c

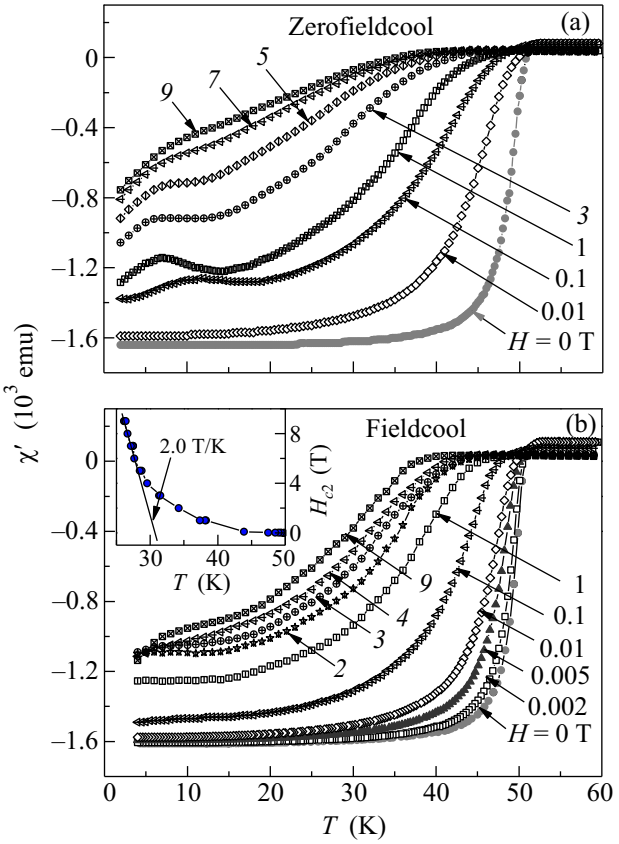

Fig.4. Temperature dependence of the real part of the magnetic susceptibility $\chi'(T)$ measured (a) for "zero field cooling" (ZFC) and (b) for "field cooling" (FC) in various magnetic fields. Field values are indicated on the figure. The insert shows temperature dependence of the critical field H_{c2}, determined from data on the main panel at the middle of the transition

and the ac-susceptibility was measured during cooling the sample in a given magnetic field.

Comparing Figs.4a and 4b, one can see that in low magnetic fields (< 0.01 T), the curves ZFC-$\chi'(T)$ and FC-$\chi'(T)$ are almost the same. This is in a sharp contrast to previous data for polycrystalline GdFeAs based superconductors from Refs. [13, 16], where almost 1:20 ratio of the ZFC to FC data was reported. Even for nominally single-crystals of $SmFeAsO_{0.6}F_{0.35}$ [14], the ratio is an order of 1:20. We believe, that the coincedence of ZFC and FC data (Figs.4a and 4b) indicates that the superconducting phase in our sample has a bulk character and constitutes almost 100% of the sample volume. In higher fields, the ZFC-$\chi'(T)$ and FC-$\chi'(T)$ behavior becomes different; we have currently no explanation for the observed unusual difference. Interestingly, $\chi'(T)$ measured in ZFC-regime demonstrates a wide peak at low temperatures (below 20 K) and in fields 0.1–9 T. This

behavior might be related with magnetic ordering of Gd ions. This effect requires further studies.

Besides T_c, another important parameter is the second critical field H_{c2}. The H_{c2} value is known to be high for FeAs-type superconductors. As an example, for $SmFeAsO_{0.7}F_{0.25}$ the measured derivative is $dH_{c2}/dT = -(2-4)$T/K [14]; this leads to a rough estimate $H_{c2} \sim 70 \div 140$T. For our "optimally dopped" $GdFeAsO_{0.88}F_{0.12}$ polycrystalline sample, the temperature derivative of the critical field dH_{c2}/dT was found from the measured $R(T,H)$ and $\chi'(T,H)$ temperature dependences. In the inserts to Fig.3 and Fig.4 we plotted the $H_{c2}(T)$ dependence, determined at the middle of the superconductiong transition from both, $R(T)$ and $\chi'(T)$ curves. From these data we obtain the slope $|dH_{c2}/dT|$ equal to 2 and 3.6 T/K, respectively. To compare with other reported data for oxipnictide superconductors, we use the latter estimate. The slope is a factor of four larger than for $LaFeAsO_{1-x}F_x$ [17], and comparable to that for optimally doped SmFeAs-based superconductors [14]. Using the conventional Werthamer-Helfand-Hohenberg BCS theory for type II superconductors [18] we obtain an estimate $H_{c2} = -0.693 T_c (\partial H_{c2}/\partial T)|_{T_c} \approx$ $\approx$ 130 T, comparable to H_{c2} for YBCO (though with $T_c = 92$ K). This estimate, of cause, will be affected by the paramagnetic limit which we currently don't now. Nevertheless, potentially high values of the critical field, up to 130 T make the Gd-FeAs superconductor interesting for practical high-field applications.

In summary, we elaborated high pressure synthesis method and synthesized several $GdFeAsO_{1-x}F_x$ single-phase polycrystalline samples with different content of oxigen and fluorine; the synthesized materials have critical temperature in the range $38-52$ K. We also found that the high-temperature synthesis in ampoules does not enable to obtain single-phase superconductors of this composition. The highest $T_c \approx 53$K was found for $GdFeAsO_{0.88}F_{0.12}$. The evidence for the single-phase superconductors is provided by the X-ray diffraction and by comparison of the temperature dependences of the magnetic susceptibility measured in "zero field cooling" and "field cooling" conditions. The "optimally doped" samples with $x = 0.12$ demonstrate high value of the derivative dH_{c2}/dT, which leads to an estimate for $H_{c2}(0)$ up to ~ 130 T.

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1. Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **30**, 3296 (2008).
2. H. Takahashi, K. Igawa, K. Arii et al., Nature **453**, 376 (2008).
3. X.H. Chen, T. Wu, G. Wu et al., Nature **453**, 761 (2008).
4. R.H. Liu, G. Wu, T. Wu et al., Phys. Rev. Lett. **101** 087001 (2008).
5. I.I. Mazin, D.J. Singh, M.D. Johannes, and M.H. Du, Phys. Rev. Lett. **101** 057003 (2008).
6. M.V. Sadovskii, Uspekhi **178**, 1243 (2008).
7. G.F. Chen, Z. Li, D. Wu et al., Phys.Rev. Lett. **100**, 247002 (2008).
8. A.A. Golubov, A. Brinkman, O.V. Dolgov et al., archive:0812.5057.
9. D. Parker, M.G. Vavilov, A.V. Chubukov, and I.I. Mazin, archive:0907.2826.
10. C.-T. Chen, C.C. Tsuei, M.B. Ketchen et al., archive:0905.3571
11. Yu.A. Izyumov and E.Z. Kurmaev, Uspekhi **178**, 1307 (2008).
12. A.L. Ivanovskii, Uspekhi **178**, 1273 (2008).
13. Peng Cheng, Lei Fang, Huan Yang et al., Science in China G **51**(6), 719 (2008).
14. J. Karpinski, N.D. Zhigadlo, S. Katrykh et al., Physica C **469**, 370 (2009).
15. http://www.hppi.troitsk.ru/our-products.htm
16. K. Miyazawa, K. Kihou, P.M. Shirage et al. J. Phys. Soc. Jp **78**, 03472 (2009).
17. A.S. Sefat, M.A. McGuire, B.C. Sales et al., Phys. Rev. B **77**, 174503 (2008).
18. E. Helfand and N.R. Werthamer, Phys. Rev. **147**, 288 (1966); N.R. Werthamer, E. Helfand, and P.C. Hohenberg, ibid, p. 295.