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FAST TRACK COMMUNICATION

Synthesis and crystal growth of $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$: a new iron-based superconductor with $T_c = 27$ K

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Abstract

We report on the synthesis of large single crystals of a new FeSe layer superconductor $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$. X-ray powder diffraction, neutron powder diffraction and magnetization measurements have been used to compare the crystal structure and the magnetic properties of $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ with those of the recently discovered potassium intercalated system $\text{K}_x\text{Fe}_2\text{Se}_2$. The new compound, $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$, shows a slightly lower superconducting transition temperature ($T_c = 27.4$ K) in comparison to 29.5 in $(\text{K}_{0.8}\text{FeSe}_{0.98})_2$. The volume of the crystal unit cell increases by replacing K by Cs—the c parameter grows from 14.1353(13) to 15.2846(11) Å. For the alkali metal intercalated layered compounds known so far, $(\text{K}_{0.8}\text{Fe}_2\text{Se}_2$ and $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$), the T_c dependence on the anion height (distance between Fe layers and Se layers) was found to be analogous to those reported for As-containing Fe superconductors and $\text{Fe}(\text{Se}_{1-x}\text{Ch}_x)$, where Ch = Te, S.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The recent discovery of Fe-based superconductors has triggered a remarkable renewed interest for possible new routes leading to high-temperature superconductivity. As observed in the cuprates, the iron-based superconductors exhibit interplay between magnetism and superconductivity, suggesting the possible occurrence of unconventional superconducting states.

Other common properties are the layered structure and the low carrier density. Among the iron-based superconductors FeSe_{1-x} has the simplest structure with layers in which Fe cations are tetrahedrally coordinated by Se [1]. The superconducting transition temperature (T_c) of 8 K was found to dramatically increase under pressure reaching a maximum of 37 K, with a rate of $dT_c/dP \sim 9.1$ K GPa⁻¹—the highest among all the Fe-based superconductors [2]. Additionally, it was found that an applied pressure modifies the electronic phase diagram of FeSe_{1-x} and induces static magnetic order

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which can coexist with superconductivity [3]. Moreover, the substitution of Te for Se leads to an increase of T_c up to 14 K [4]. Since Te is larger than Se, this effect could not be considered as corresponding to an externally applied pressure. It was also found that substitution of S for Se increases T_c slightly [5]. Comprehensive studies of substitutions on the iron site in $M_x\text{Fe}_{1-x}\text{Se}_{0.85}$ with the non-transition metals $M = \text{Al}, \text{Ga}, \text{In}, \text{Sm}, \text{Ba}$ and transition metals $M = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Co}, \text{Ni}$ and Cu , were performed by Wu *et al* [6]. In the first case it was stated that the observed slight change of T_c (within ± 2 K) depends on the size of the substituting ions and the doping level, suggesting the importance of the lattice deformation on the superconducting properties. All the systems with transition metals (with the exception of Mn) do not exhibit superconductivity. In the case of $M = \text{Cu}$ already 1.5% of doping suppresses superconductivity [7] and with 10% the compound becomes a Mott insulator [8]. Transition metal doping was also reported in the case of $\text{Fe}_{1-x}\text{Se}_{0.5}\text{Te}_{0.5}$. Doping with Co ($0.05 \leq x \leq 0.2$) and Ni ($0.05 \leq x \leq 0.1$) both suppress T_c and lead to a metal–insulator transition [9]. Doping with Cu ($x = 0.05$) destroys superconductivity whereas magnetic Mn ($x = 0.05$) slightly increases T_c [10]. The alkali-metal-doped $\text{Na}_{0.1}\text{FeSe}$, where the Na ions are intercalated between FeSe layers, was found to be superconducting with $T_c = 8.3$ K [11].

Very recently superconductivity at above 30 K was found in $\text{K}_{0.8}\text{Fe}_2\text{Se}_2$ [12]. This is, so far, the highest T_c for Fe-chalcogenides, even though the superconducting fraction is low and the transition is broad. It is also reported [12] that single crystals of several mm^3 could be grown from the self-flux. This new compound is isostructural to layered (122-type) iron pnictides with the space group $I4/mmm$ [13].

This structure has the same FeSe layers as in (11) FeSe [14], but in (11) FeSe with space group $P4/nmm$ these layers are identical with respect to the translation along the z direction (this is obvious, because the unit cell contains only one FeSe layer). In $\text{K}_{0.8}\text{Fe}_2\text{Se}_2$ the unit cell is doubled along the z axis. The neighboring FeSe layers along the z direction are shifted by $(1/2, 1/2, 1/2)$, so that the upwards SeFe_4 pyramid is faced with the downwards pyramid along the z direction and the intercalated atom is located between more distant Se atoms along z . The Fe–Fe layer distance in $\text{K}_{0.8}\text{Fe}_2\text{Se}_2$ increases to 7.0184 Å in comparison with 5.5234 Å in FeSe [14]. The intercalation of K also increases the Fe–Se bond length within the layers by 2.15%.

In the present work we report on the synthesis and crystal growth of a new analog compound with Cs intercalated between FeSe layers. In comparison with the work of Guo *et al* [12] we managed by this substitution to significantly increase the superconducting fraction by only slightly diminishing the critical temperature.

2. Experimental details

Single crystals of both potassium and cesium intercalated iron selenides of nominal compositions $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ and $\text{K}_{0.8}(\text{FeSe}_{0.98})_2$ were grown from the melt using the Bridgeman method. Ceramic rods of the iron selenide starting material

were prepared by the solid state reaction technique [14]. The nominal stoichiometry of the starting material that is $\text{FeSe}_{0.98}$ was chosen based on the view of our previous studies [14] which demonstrated that for this particular Fe/Se ratio the content of secondary phases is the smallest. High purity (at least 99.99%, Alfa) powders of iron and selenium were mixed in an 8 g batch, pressed into rods, sealed in evacuated quartz ampoules and annealed at 700 °C during 15 h. The initially treated material was then ground in an inert atmosphere, pressed again into rods, sealed in evacuated quartz ampoules and thermally treated at 700 °C over 48 h followed by further annealing at 400 °C for another 36 h.

For the single-crystal synthesis a piece of the ceramic rod of $\text{FeSe}_{0.98}$ was sealed in a double-wall evacuated silica ampoule with the pure alkali metals (either potassium or cesium of at least 99.9% purity, Chempur). The quantity of alkali metal used for the synthesis depended on the desired stoichiometry of the final compound. The ampoules were annealed at 1030 °C over 2 h for homogenization. Afterwards the melt was cooled down to 750 °C at the rate of 6 °C h^{-1} and then cooled down to room temperature at the rate 200 °C h^{-1} . Well-formed black crystal rods of 7 mm diameter (diameter of the quartz ampoules) were obtained which could be easily cleaved into plates with flat shiny surfaces.

The $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$ and $\text{K}_{0.8}(\text{FeSe}_{0.98})_2$ crystals were characterized by powder x-ray diffraction (XRD) using a D8 Advance Bruker AXS diffractometer with Cu $K\alpha$ radiation. For these measurements a fraction of each crystal was cleaved, powderized, and loaded into the low background airtight specimen holder in an He glove box to protect the powder from oxidation. The $\text{K}_{0.8}(\text{FeSe}_{0.98})_2$ polycrystalline sample, which was synthesized the same way as proposed by Guo *et al* [12], was additionally studied by means of neutron powder diffraction (NPD) at the SINQ spallation source of the Paul Scherrer Institute (PSI, Switzerland) using the high-resolution diffractometer for thermal neutrons, HRPT [15], with the neutron wavelengths $\lambda = 1.494$ and 1.886 Å. The sample was loaded into a vanadium container with an indium seal in an He glove box. The refinements of the crystal structure parameters were done using the FULLPROF program [16] with the use of its internal tables.

The superconducting transition has been detected by AC susceptibility by using a conventional susceptometer. The sample holder contains a standard coil system with a primary excitation coil (1300 windings, 40 mm long) and two counterwound pick-up coils (reference and sample coil, each 10 mm long and 430 windings) which are connected to a lock-in amplifier. The frequency used was 144 Hz and the sample holder diameter was 5 mm. Measurements were performed by heating the sample at a rate of 9 K h^{-1} . The susceptometer was calibrated using the superconducting transition of a lead sample showing a 100% superconducting fraction. The raw data were then normalized to the sample volume relative to the one of the Pb calibration specimen.

3. Results and discussion

Room-temperature XRD experiments revealed that the crystals do not contain any impurity phases. The only detected

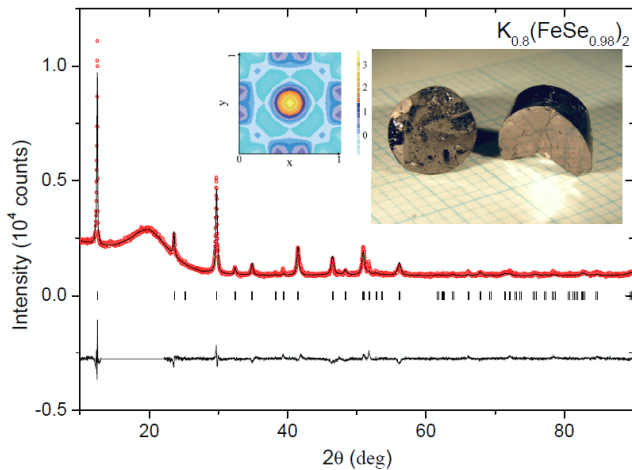


Figure 1. Rietveld refinement pattern (upper—red) and difference plot (lower—black) of the x-ray diffraction data for the crystal with the nominal composition of $K_{0.8}(FeSe_{0.98})_2$. The rows of ticks show the Bragg peak positions for the $I4/mmm$ phase. The left insert shows the difference Fourier density map at $z = 1/2$ slice obtained from NPD data showing the presence of K at (0.5, 0.5, 0.5), while the colored scale shows scattering density in fm. The right insert shows a picture of the cleaved $K_{0.8}(FeSe_{0.98})_2$ crystal.

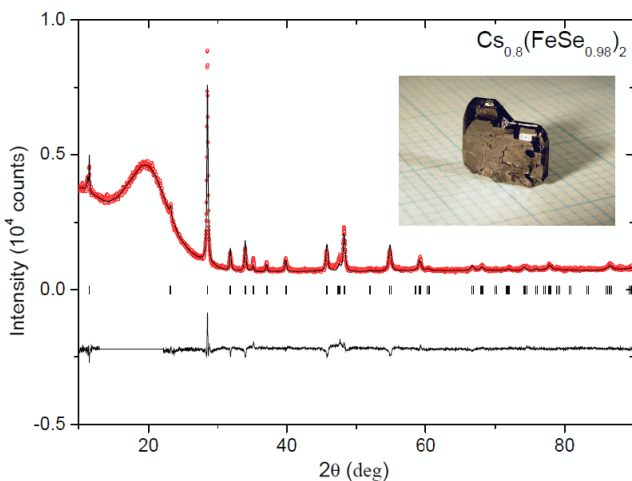


Figure 2. Rietveld refinement pattern (upper—red) and difference plot (lower—black) of the x-ray diffraction data for the crystal with the nominal composition of $Cs_{0.8}(FeSe_{0.98})_2$. The rows of ticks show the Bragg peak positions for the $I4/mmm$ phase. The inset shows a picture of a piece of $Cs_{0.8}(FeSe_{0.98})_2$ crystal.

phase is the tetragonal phase of $ThCr_2Si_2$ type (space group $I4/mmm$). The results of the Rietveld refinement of the XRD patterns are shown in figures 1 and 2 for $Cs_{0.8}(FeSe_{0.98})_2$ and $K_{0.8}(FeSe_{0.98})_2$, correspondingly. The broad halo on the XRD pattern around 20° is caused by a sample holder with a plastic dome. This area was excluded from the refinements. For the refinement it was assumed that all Fe and Se sites are fully occupied. The crystallographic data for $Cs_{0.8}(FeSe_{0.98})_2$ and $K_{0.8}(FeSe_{0.98})_2$ crystals and $K_{0.8}(FeSe_{0.98})_2$ polycrystalline are summarized in table 1.

One can note that the atomic displacement parameters (ADP) refined from XRD are quite large in comparison with

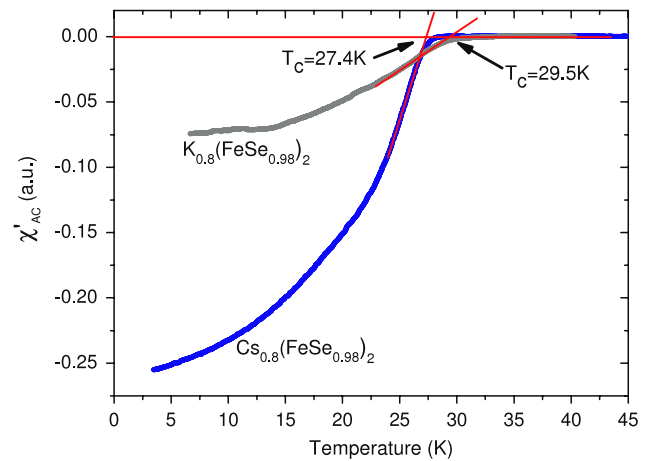


Figure 3. Temperature dependence of the AC susceptibility (χ') for single-crystalline $K_{0.8}(FeSe_{0.98})_2$ and $Cs_{0.8}(FeSe_{0.98})_2$. The signal has been normalized to a superconducting Pb specimen as described in the text.

Table 1. Structural parameters for $Cs_{0.8}(FeSe_{0.98})_2$ and $K_{0.8}(FeSe_{0.98})_2$ powderized crystals and $K_{0.8}(FeSe_{0.98})_2$ powder at 290 K obtained from XRD and NPD, correspondingly. Space group $I4/mmm$ (no. 139), Fe in (4d) position (0, 0.5, 0.25); Se in (4e) position (0, 0, z), Cs/K in (2a) position (0, 0, 0). The atomic displacement parameters (represented by the B parameter) for all atoms were constrained to be the same.

	$Cs_{0.8}(FeSe_{0.98})_2$ (XRD) powderized crystal	$K_{0.8}(FeSe_{0.98})_2$ (XRD) powderized crystal	$K_{0.8}(FeSe_{0.98})_2$ (NPD) polycrystalline
a (Å)	3.9601(2)	3.9092(2)	3.9038(1)
c (Å)	15.2846(11)	14.1353(13)	14.1148(6)
Se, z	0.3439(3)	0.3503(3)	0.3560(3)
Cs/K	0.771(7)	0.792(10)	0.737(20)
occupancy			
B (Å ²)	3.37(9)	3.16(9)	1.63(4)
R_p, R_{wp}, R_{exp}	4.35, 6.00, 3.09	3.84, 5.10, 2.99	4.91, 6.71, 3.25
χ^2	3.77	2.90	4.26

the ones refined from NPD. We believe that this results from a slight degradation of the samples during the XRD measurements due to the non-ideal sealing of the plastic container, inasmuch as the samples are extremely air-sensitive. It is also supported by the fact that both samples show a pronounced strain-like diffraction peak broadening. The enhanced ADP can lead to systematic errors in determination of the site occupancies. The substitution of Cs for K causes the lattice to expand predominantly in the c direction, due to the larger ionic radius of Cs (1.78 Å) compared to K (1.51 Å).

Figure 3 shows the temperature dependence of the AC susceptibility (χ') for single crystals of $K_{0.8}(FeSe_{0.98})_2$ and $Cs_{0.8}(FeSe_{0.98})_2$. The onset of the critical temperature has been determined to be $T_{c,onset} = 27.4$ K and 29.5 K for the Cs and K intercalated compounds, respectively. It has to be noted that the diamagnetic signal is larger in the case of the Cs-intercalated FeSe, which might point to a bigger Meissner fraction. A further investigation if this effect is intrinsic to the $K_{1-x}(FeSe_{0.98})_2$ and $Cs_{1-x}(FeSe_{0.98})_2$ families

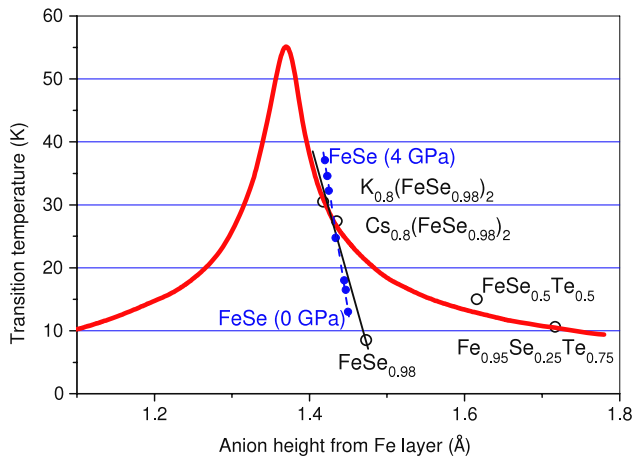


Figure 4. Dependence of T_c on the distance between Fe and the chalcogenide/pnictide layers. The red line shows the dependence as presented by Mizuguchi *et al* [17] for typical Fe-based superconductors. The filled circles indicate the data obtained for FeSe under high pressure [2]. The open points indicate the data obtained by this work and our previous reports [18, 19].

or if the superconducting fraction sensitively depends on the composition x is underway.

Intercalation of the alkali metals into the FeSe causes serious structural changes. It was proved by Mizuguchi *et al* [17] that in iron pnictides and chalcogenides the critical temperature can be correlated with the so-far known ‘anion height’, which is the distance between Fe and chalcogenide (or pnictide) layers in the structure. Figure 4 presents a line (taken from [17]) being a best fit to the experimental data obtained for over 15 differed Fe-based superconducting compounds. The curve shows a relatively sharp peak around 1.38 Å with a maximum transition temperature $T_c \approx 55$ K (for NdFeAsO_{0.83}). The open symbols in figure 4 depict the anion height to T_c correlation of the samples synthesized in this work and those presented in our previous reports [18, 19]. Apparently the newly synthesized compounds with intercalated Cs and K follow very well the universal trend. The tendency in the series FeSe_{0.98}–Cs_{0.8}(FeSe_{0.98})₂–K_{0.8}(FeSe_{0.98})₂ is analogous to that reported for high pressure measurements [2] (filled circles in figure 4). The steep slope of T_c as a function of anion height suggests that even much higher superconducting transition temperatures might be found in the newly discovered FeSe-based systems by applying either chemical (substitutional) or hydrostatic pressures. Another not yet explored aspect is the relation of magnetism and superconductivity in this system. Anyhow, whether or not superconductivity appears in this system in close proximity to an antiferromagnetically ordered state like in other Fe-based superconductors awaits further investigation. Fortunately, the synthesis method described here is able to provide large single crystals which will allow us to answer the above questions

in detail by applying bulk methods like neutron scattering or muon spin rotation, both at ambient and high pressures.

4. Summary

In conclusion, a new Cs intercalated iron selenide superconductor (Cs_{0.8}(FeSe_{0.98})₂) was synthesized by the Bridgeman method in the form of large single crystals. The Cs_{0.8}(FeSe_{0.98})₂ compound represents the second member of the alkali metal chalcogenide family. In comparison with the K-analog a larger lattice volume is observed and $T_{c,onset} = 27.4$ K is only slightly decreased compared to K_{0.8}Fe₂Se₂. The large high quality crystals obtained by the method described will allow an in-detail study of fundamental magnetic and superconducting properties in this new FeSe family.

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