FAST TRACK COMMUNICATION

Structural and magnetic phase transitions in triclinic Ca_{10}(FeAs)_{10}(Pt_{3}As_{8})

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Abstract
We report the structural and magnetic phase transitions of triclinic Ca_{10}(FeAs)_{10}(Pt_{3}As_{8}), which is the parent compound of the 1038-type iron–arsenide superconductors. High-resolution x-ray diffraction reveals splitting of the in-plane (a, b) lattice parameters at \( T_s \approx 120 \text{ K} \). Platinum-doping weakens the distortion and shifts the transition temperature to 80 K in Ca_{10}(Fe_{1-x}Pt_{x}As)_{10}(Pt_{3}As_{8}) with \( x = 0.03 \). µSR experiments show the onset of magnetic order near \( T_s \) and a broad magnetic phase transition. The structural transition involves no reduction of the space group symmetry in contrast to the other parent compounds of iron–arsenide superconductors; nevertheless the local fourfold symmetry of the FeAs-layers in Ca_{10}(FeAs)_{10}(Pt_{3}As_{8}) is broken.

(Some figures may appear in colour only in the online journal)

1. Introduction

Superconductivity in iron–arsenides emerges from stoichiometric parent compounds in the course of the destabilization of antiferromagnetic ground states by chemical doping or pressure [1, 2]. The stripe-type antiferromagnetic ordering of the 1111-, 122-, and 111-type iron–arsenides is linked to an orthorhombic distortion of the tetragonal lattice, which occurs at a temperature \( T_N \) slightly above the Néel-point \( T_N \) [3–7]. This proximity of superconductivity to the structural and magnetic phase transition was not clearly evidenced in the more complex iron–arsenide superconductor Ca_{10}(Fe_{1-x}Pt_{x}As)_{10}(Pt_{3}As_{8}) [8–10]. Their crystal structures contain alternating layers of iron–arsenide and platinum–arsenide, each separated by calcium atoms as shown in figure 1.

The compound referred to as the 1038 phase contains Pt_{3}As_{8}-layers, while in the 1048 phase one more platinum atom is located in Pt_{4}As_{8}-layers. Superconductivity in 1038-/1048-compounds is controlled by Pt-doping at the iron-sites or by doping with excess electrons either from the Pt_{4}As_{8}-layer or from La-doping at the Ca-sites. High critical temperatures up to 38 K only occur with clean FeAs-layers, while \( T_c \) remains below 15 K with Pt-doped layers [11]. This doping behavior is similar to the other FeAs-superconductors, where transition metal doping induces significantly lower critical temperatures than electron- or hole-doping outside the FeAs-layers. Electronic structure calculations [8] as well as angle-resolved photoemission experiments [12] have shown that the Fermi surface of the 1038-/1048-superconductors exhibits features very similar to the simpler FeAs compounds.

Thus far there is every indication that the 1038-/1048-materials act according to the same principle as known FeAs-superconductors. Therefore a non-superconducting parent compound with antiferromagnetic ordering and a structural phase transition should exist. Recently we have proposed the stoichiometric 1038 phase Ca_{10}(FeAs)_{10}(Pt_{3}As_{8}) as the parent compound [11]. By assigning the usual ionic
Figure 1. (a) Crystal structure of Ca$_{10}$(Fe$_{1-x}$Pt$_x$As)$_{10}$(Pt$_3$As$_8$) ($x = 0, 0.03$), (b) Pt$_3$As$_8$ layer, (c) FeAs-layer with the in-plane lattice translations $a$, $b$.

charges according to Ca$_{10}^+$[(FeAs)$_{10}^-$(Pt$_3$As$_8$)$_{10}^-$] we obtain the identical charge for the FeAs-layer ($-1$) as in the 1111- or 122-type parent compounds. Moreover, we found that superconductivity is induced from this stoichiometric 1038 phase by La-doping at the Ca-site [11]. Thus one also expects an antiferromagnetic ground state of non-superconducting Ca$_{10}$(FeAs)$_{10}$(Pt$_3$As$_8$) and consequently a structural distortion of the FeAs-layer. The latter was also suggested on the base of polarized light imaging [13]. A recent preprint [14] reported the phase diagram of the La-doped 1038 phase and assumed the existence of structural and magnetic transitions from weak features in the magnetic susceptibility, specific heat, and kinks in the derivative of the electrical resistivity. Another preprint [15] reported evidence for antiferromagnetic ordering in the 1038 phase from $^{75}$As NMR data. All reports so far generally support the existence of a structural transition in the 1038 compound, but none of them gives clear experimental evidence of a lattice distortion.

In this letter we show that the non-superconducting 1038 phase undergoes a structural phase transition near 120 K. The splitting of the equal in-plane lattice parameters $a$, $b$ in the triclinic crystal structure is observed by high-resolution x-ray diffraction. Concomitant magnetic ordering is proved by means of $\mu$SR data showing an onset of magnetic ordering near $T_s$, followed by a broad magnetic transition.

2. Experimental details

Polycrystalline samples of platinum iron–arsenides were synthesized as described in [11], and characterized by x-ray powder diffraction using the Rietveld method with TOPAS [16]. Compositions were determined within errors of ±10% by refining occupation parameters and by x-ray spectroscopy (EDX). Temperature-dependent x-ray powder diffraction data were collected using a HUBER G670 Guinier imaging plate diffractometer (Cu $K\alpha$ radiation, Ge-111 monochromator) equipped with a close-cycle He-cryostat. De-resistivity was measured on a cold pressed pellet which had been annealed at 1073 K for 20 h. Magnetic susceptibility was measured using a Quantum Design MPMS-XL5 SQUID magnetometer. $\mu$SR measurements were performed using the GPS and Dolly spectrometers located at the $\pi$M3 and $\pi$E1 beamlines of the Swiss Muon Source at the Paul Scherrer Institut, Switzerland. The data were analyzed using the MUSRFIT package [17].

3. Results and discussion

Figure 2 shows the x-ray powder pattern of Ca$_{10}$(FeAs)$_{10}$(Pt$_3$As$_8$) measured at 10 K together with the Rietveld fit. Only small amounts of FeAs (4%) were detected as impurities. Temperature-dependent changes in the pattern are tiny, and the splitting of the lattice parameters $a$, $b$ becomes visible only at certain high angle reflections. The inset in figure 2 shows a double peak, mainly generated by the (262)- and (620)-reflections. While the position of the (620)-peak is almost constant near 80.55°, the (262)-peak begins to shift to higher angles as the temperature drops below 100 K, and is clearly discernible to the right of the (620)-reflection at 10 K.

Figure 3 shows the temperature dependency of the lattice parameters refined from x-ray powder data for Ca$_{10}$(Fe$_{1-x}$Pt$_x$As)$_{10}$(Pt$_3$As$_8$) with $x = 0$ and 0.03, and optimally La-doped (Ca$_{0.85}$La$_{0.15}$)$_{10}$(FeAs)$_{10}$(Pt$_3$As$_8$) for
comparison. Within the accuracy of the method, the lattice parameters $a$ and $b$ are equal at ambient temperature, due to the square base planes of both the FeAs- and Pt$_3$As$_8$-layers. The $c$-axis decreases monotonically with cooling, while the angles remain nearly constant. The stoichiometric and underdoped 1038 compounds exhibit lattice distortions at 120 K and 80 K, respectively. Similar properties are known for a variety of iron–arsenide compounds like BaFe$_2$As$_2$, where the phase transition results in a symmetry reduction from tetragonal $I4/mmm$ to orthorhombic $Ibam$ [5], or LaOFeAs with a transition from $P4/nmm$ to $Cmme$ [18]. The triclinic structure of the 1038 compounds precludes further reduction of the lattice symmetry, thus the transformation is isostructural. Nevertheless, the phase transition is tied to the loss of the local fourfold symmetry in the FeAs-layer, which is the crucial effect with respect to the physical properties.

The resistivity measurement is displayed in figure 4. The semiconductor-like development to low temperatures is in contradiction to known iron–arsenides, but was recently also observed by Xiang et al [19]. Absolute resistivity values are in the typical range for iron pnictides. The derivatives of resistivity data with respect to temperature reveal an anomaly near 120 K, coinciding for heating and cooling measurements.

Muon spin rotation experiments with stoichiometric Ca$_{10}$(FeAs)$_{10}$(Pt$_3$As$_8$) detected three different muon precession frequencies with constant ratios, which accounts for three different muon sites in the magnetic unit cell of the homogeneous phase. The onset of long-range magnetic order below 130 K was found in transverse field (TF) and zero field (ZF) $\mu$SR data; inset: ZF-$\mu$SR spectra of Ca$_{10}$(FeAs)$_{10}$(Pt$_3$As$_8$) at different temperatures. The magnetic susceptibility of Ca$_{10}$(FeAs)$_{10}$(Pt$_3$As$_8$) (figure 6) shows a weak and broad anomaly in the temperature region of the structural transition, in agreement with [14], thus substantiating a gradual development of magnetic order.

The origin of the additional feature near 170 K is still
unclear and has also been observed in [14]. The linear magnetization isotherm at 1.8 K (not shown) is compatible with antiferromagnetic order. The field dependency and the upturn of the susceptibility at low temperatures indicates a trace of ferromagnetic impurity in the sample, which is not detectable in the x-ray powder pattern. From the results so far, we suggest a magnetic ordered state similar to the parent compounds BaFe$_2$As$_2$ or LaOFeAs. However, the low space group symmetry allows deviations from the stripe-type pattern, which remains to be seen.

4. Conclusion

In summary, our results give clear evidence for the magnetic and structural phase transition of Ca$_{10}$(FeAs)$_{10}$(Pt$_3$As$_8$) to an antiferromagnetic low-temperature phase at $T_s \approx 120$ K. In contrast to the 1111- and 122-type iron--arsenides, the phase transition involves no reduction of the space group symmetry. Nevertheless the local tetragonal symmetry in the FeAs-layers is broken. The magnitude of the lattice distortion is roughly half that observed in BaFe$_2$As$_2$ in terms of the order parameter $\delta = (a-b)/(a+b)$, and decreases with Pt-doping on the Fe-sites, as expected. Finally the transition is completely suppressed in optimally doped La-1038. The onset of long-range magnetic order in Ca$_{10}$(FeAs)$_{10}$(Pt$_3$As$_8$) coincides with the structural distortion at $T_s \approx 120$ K. In contrast to BaFe$_2$As$_2$, the magnetic fraction develops gradually and does not reach 100% until 5 K. Taking this together with the temperature-independent $\mu$SR frequencies, a gradual increase of the structurally distorted compound at the expense of the ambient temperature phase should be observable below 130 K. However, our low-temperature structural data suggest a rather sharp structural change in the whole sample, without coexistence with the undistorted phase. While the detailed nature of the phase transition necessitates further investigations, our results demonstrate that the 1038 material acts according to the same principle as the known FeAs-superconductors with Ca$_{10}$(FeAs)$_{10}$(Pt$_3$As$_8$) as the parent compound.

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