Thermodynamic evidence for pressure-induced bulk superconductivity in the Fe–As pnictide superconductor CaFe$_2$As$_2$

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Abstract. We report on specific-heat and resistivity experiments performed in parallel in a Bridgman-type pressure cell in order to investigate the nature of pressure-induced superconductivity in the iron pnictide compound CaFe$_2$As$_2$. The presence of a pronounced specific-heat anomaly at $T_c$ reveals the bulk nature of the superconducting state. The thermodynamic transition temperature differs dramatically from the onset of the resistive transition. Our data indicate that superconductivity occurs in the vicinity of a crystallographic phase transition. We discuss the discrepancy between the two methods as caused by strain-induced superconducting precursors formed above the bulk thermodynamic transition due to the vicinity of the structural instability.

With the recent discovery of iron pnictide superconductors [1], the phenomenon of high-temperature superconductivity is no longer limited to cuprate materials. Having two distinct high-temperature superconducting families represents a great opportunity to gain new insights into the mechanism of high-temperature superconductivity. In contrast to the antiferromagnetic Mott insulators of the cuprates parent compounds, those of the pnictide superconductors show spin density wave (SDW) magnetism (for a review see [2]), although it is still debated whether

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the nature of magnetism is itinerant or localized [3–5]. Superconductivity is mainly associated with the Fe–As layers and appears close to the border of the antiferromagnetically ordered SDW phase [2, 6]. A maximum $T_c$ of 55 K has been observed in the ‘1111’ structural family of the electron-doped ReOFeAs compounds (Re: rare earth) [7]. Further classes of materials are the self-doped ‘111’ compounds (AFeAs, where A = alkaline) and the hole-doped ‘122’ compounds based on the MFe$_2$As$_2$ parent compound (M: Ba, Sr, Ca, K, Rb and Cs) with $T_c$ values of up to 38 K for K-doped BaFe$_2$As$_2$ and SrFe$_2$As$_2$ [8, 9]. The 122 family is particularly interesting for detailed studies of the pnictides phase diagram as large single crystals are available and the parent compound can be doped on the M site [10–12], the Fe site (Co) [13] or the As site (P) [14], or by the application of pressure ([15]; for a review see [16]), not to mention the appearance of superconductivity in the undoped compounds under micrographic strain [17]. Doping charge carriers suppresses the magnetic SDW transition, which more or less coincides with a structural transition from a low-temperature orthorhombic (O) to a tetragonal (T) phase. CaFe$_2$As$_2$ (Ca122) is the member with the smallest unit cell volume, and moderate pressure in the kbar range is sufficient to induce superconductivity and a collapsed tetragonal (cT) phase in the parent, undoped compound [15, 16, 18, 19]. Recently, relatively high superconducting transition temperatures were reported in hole-doped (Ca$_{1-x}$Na$_x$)Fe$_2$As$_2$ (above 33 K) [9] and in electron-doped (Ca$_{1-x}$Pr$_x$)Fe$_2$As$_2$ with $T_c$ values up to 49 K [10, 11]. This motivates further research to better understand the mechanism of superconductivity and the exact phase diagram in the parent undoped compound Ca122 under pressure, especially because it has been suggested that a giant coupling of the on-site Fe-magnetic moment with the As–As bonding along the $z$-axis may provide a mechanism for unconventional superconductivity in the 122 materials [20].

Besides the O-to-T structural phase transition, which is suppressed at a relatively low pressure, a further structural transition from the T to the cT phase occurs at higher pressures [19]. The transition is associated with a drastic reduction in the $c/a$ ratio. Pressure-induced superconductivity in Ca122 is complicated by the fact that it occurs in the vicinity of the pressure-induced structural transition from the O to the cT phase. Theoretical investigations indicated that all structural transitions in Ca122 are strongly coupled to electronic degrees of freedom and are accompanied by a pronounced change of the Fermi surface [21, 22]. Therefore, the presence of even small pressure gradients in the experiment may strongly influence the structural, electronic and superconducting properties [23]. The exact nature of pressure-induced superconductivity is hence strongly debated: in susceptibility and transport studies under hydrostatic pressure with helium as a pressure medium an exceptionally sharp transition from the O phase to the non-magnetic cT phase has been found. At low temperatures only a very weak drop of resistivity has been observed without any feature in susceptibility, which suggests the absence of bulk superconductivity under purely hydrostatic conditions [24]. It has been proposed that, in order to observe pressure-induced superconductivity in Ca122, a certain uniaxial pressure component is required to stabilize a tetragonal phase at low temperatures which may coexist with other structural phases [25]. It has furthermore been argued that superconductivity under non-hydrostatic conditions may originate from the presence of a strain-induced multi-crystallographic mixed phase [19, 26]. Superconductivity has been proposed to be associated with domain walls between highly phase-separated regions of different structures [24]. In this scenario, superconductivity would be of a filamentary nature. AC-susceptibility measurements under pressure indicated, however, that under quasi-hydrostatic conditions a considerable volume fraction of the samples becomes superconducting [26].
In contrast to measurements of the electrical resistivity and magnetic susceptibility, which are often misled by filamentary or surface superconductivity [27], the specific heat is a true bulk thermodynamic method and perfectly suited for investigating whether pressure-induced superconductivity in Ca122 is of bulk nature. Furthermore, it represents an ideal tool to investigate pressure-induced structural phase transitions. Measurement of the specific heat under pressure is difficult due to the need to thermally isolate the sample. In this paper, we present specific-heat data under pressure up to 20 kbar on a single crystal of Ca122 under quasi-hydrostatic conditions. As we will show, the observation of a pronounced specific-heat anomaly clearly indicates bulk superconductivity. The measurements, furthermore, provide details of the structural transitions upon approaching the superconducting phase and reveal a strong difference between the thermodynamics and the resistive determination of the superconducting transition temperature.

Single crystals of Ca122 have been grown from self-flux as described in detail elsewhere [11]. Specific-heat measurements have been made in a Bridgman-type pressure cell by the same method as that used before for cuprate superconductors [28], with steatite as the pressure medium. The materials for the different components of the pressure cell have been chosen to carefully compensate for the thermal expansion of the cell in order to ensure a constant pressure during temperature sweeps. Steatite (which is also called ‘soap stone’) is less hydrostatic than commonly used liquid pressure media such as pentane–isopentane or Daphne oil 7373 [29], but has nevertheless rather good quasi-hydrostatic conditions and a great advantage over most of the liquid media (especially the most hydrostatic medium helium) that it is easier to achieve isolating the sample thermally from its surroundings by an ac modulated-temperature specific-heat technique at fast modulation. The drawback is that, in the presence of structural transitions which may be sensitive to non-hydrostatic pressure components, the phase diagram may be modified somewhat. On the other hand, as steatite is solid from the beginning, we avoid the additional stress induced upon cooling a liquid pressure medium through its solidification transition. Furthermore, it has been shown that under purely hydrostatic conditions Ca122 does not exhibit bulk superconductivity [24]. In order to investigate the pressure-induced superconductivity we therefore need to induce a certain non-hydrostaticity.

In figure 1, we present a photograph of the experiment mounted within a pyrophyllite (Al₂Si₄O₁₀(OH)₂) gasket (gray ring) on one of the tungsten carbide anvils of the Bridgman pressure cell. Ten grooves have been cut by hand into the gasket with the help of a razor blade with embedded gold wires as electrical feedthroughs. The white background within the gasket is one disc of steatite on which the experiment has been mounted. The larger lower left black rectangle represents the Ca122 single crystal which has been polished from both sides down to a thickness of 20 µm. The thin gray strip on the upper left is a thin Pb foil in a four-wire electrical configuration. The superconducting transition of lead is pressure dependent and, with the help of the literature data [30]⁴, it serves as a sensitive manometer. The sample is contacted with thin gold wires for the measurement of electrical resistivity in four-wire configuration, as well as with one AuFe/chromel and one chromel/constantan thermocouple for the heat-capacity measurements. After completion of the experimental setup a second disc has been put into the gasket to cover the experiment. The volume of the steatite is chosen to fill two-third of the volume within the gasket to reach optimal quasi-hydrostatic conditions. The gold wires in

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⁴ The pressure calibration for Pb manometers from [30] was recently confirmed up to 10 GPa by Deemyad [31] under optimal hydrostatic conditions with 4He as a pressure transmitting medium, in contrast to the data by Bireckhoven et al [32] showing deviations in the pressure range below 10 GPa.
Figure 1. Photograph of the experiment mounted within the pyrophyllite gasket of a Bridgman-type pressure cell with a solid pressure transmitting medium, as taken through a microscope. The cell is shown before the second steatite disc had been placed in the gasket. The upper left thin strip represents the Pb manometer, and the lower right black rectangle is the sample of Ca122.

the grooves were insulated electrically by pyrophyllite powder which was pushed into the grooves over the gold wires. The anvil was put into the cylindrical body of the pressure cell and the gasket was squeezed between two anvils in order to apply the pressure.

The electrical resistivity was measured with a Keithley™ 6221 ac-current source in combination with a digital lock-in amplifier. The frequency was chosen as a few Hz in order to minimize phase shifts due to dissipation or capacitive effects. For the heat-capacity measurement we sent an ac current through one of the two thermocouples and used its contact resistant as a local Joule heater in order to periodically modulate the sample temperature. The second thermocouple was used as a sensor and both the amplitude and phase shift of the thermocouple was measured with a lock-in amplifier. A standard model of ac calorimetry [33] relates the amplitude and phase shift of the induced temperature modulation $T_{ac}$ to the heat capacity ($C$) of the sample and the thermal conductance ($K$) between the sample and the heat bath (which is represented by the anvils).

$$T_{ac} = P_0/[K + i\omega C].$$

$P_0$ is the heating power provided to the sample. If the frequency $\omega$ of the temperature modulation is chosen sufficiently high (typically 200 Hz–1 kHz), the heat capacity term dominates and the thermal conductance can be neglected in a good approximation. Note that this model is too simple to exactly model the heat flow within the pressure cell. Furthermore, it is impossible to separate the heat capacity of the sample from that of the surrounding pressure...
transmitting material. For this reason, we do not attempt to extract absolute values of the specific heat but investigate relative changes in the heat capacity in the vicinity of thermodynamic phase transitions. Although the heat-capacity data are presented in arbitrary units, the data are normalized by the exact heating power provided and therefore allow us to compare the magnitude of the heat-capacity data taken under different pressures.

Figure 2 shows the electrical resistance and the specific heat of Ca122 at various applied pressures. The resistance data have been normalized by its value at 15 K. The variation of the 15 K resistivity with pressure is included in absolute values in figure 3. A broad drop to zero resistance is seen for 1 kbar pressure below 12 K, which was measured just after closing the pressure cell. For technical reasons we applied in the following a pressure of 24 kbar and measured all further data upon gradually releasing the pressure. A very weak downturn of the resistance starts to become visible in 19 kbar, which becomes more and more pronounced at lower pressure. Apart from the data at the low initial pressure of 1 kbar, no zero resistance is reached down to the lowest accessible temperature of 2 K. The onset of the downturn varies only between 11 K (highest pressure) and 12 K (lowest pressure). The dropping resistance below 11–12 K certainly indicates the presence of superconducting correlations in the pressure range between 1 and ~20 kbar and shows that an (at least percolative) path of zero resistivity is found in 1 kbar.

The absence of zero resistivity at higher pressure has been observed before, although in our case this occurs already at comparatively low pressure. This could be related to the loss of a percolative path related to structural phase separation. However, as the specific-heat anomaly indicates that a major part of the sample’s volume is superconducting in this pressure range, this is unlikely. Most of our data have been recorded upon decreasing the pressure. We have observed a similar behavior previously in cuprate superconductors, where zero resistivity was lost upon releasing the pressure, whereas the specific heat still indicated a bulk superconducting state. Therefore we attribute this behavior rather to micro-cracks in the sample which cause dissipation in the superconducting state. The presence of micro-cracks is, however, not expected to influence the specific heat.

Resistivity does not provide information on the establishment of bulk superconductivity. In the specific heat at 1 kbar a small broad jump centered around 7.7 K is found. Its magnitude represents only 3% of the total specific heat. For clarity we subtracted a phonon background in the inset of figure 2. The phonon background estimation was extracted from data taken in 24 kbar, where the sample is in the normal metallic state at all temperatures. The smallness of the jump at this pressure may indicate that only a fraction of ~5–10% of the sample’s volume is superconducting. Although its magnitude is small, a visible anomaly in this bulk thermodynamic quantity cannot be attributed to a filamentary type of superconductivity, which would be associated with a negligible volume fraction of the sample only. Between 1 and 7 kbar the jump sharpens and grows to a size of ~1/3 of the total specific-heat magnitude ($T_c = 6.9$ K). As the specific heat probes the entire volume of the sample, this clearly indicates a bulk superconducting state. The temperature range is limited here to 8.7 K as this represented the final measurement of the series during which an electrical contact was lost.

In 9 kbar several anomalies appear in the specific heat. A large peak appears at 9.4 K with a pronounced shoulder around 7.6 K. A similar step-like anomaly as in the lower pressure is centered around 5.7 K. The onset of the peak-like anomaly falls together with the downturn of the resistivity at 12 K and the anomaly extends over the temperature range where the resistivity drops. From the comparison with the resistivity it is clear that the entire anomaly is somehow...
Figure 2. (a) Electrical resistance of Ca122 for various applied pressures between 1 and 24 kbar. The data have been normalized at 15 K for clarity. The inset shows an enlargement on the onset of the superconducting transition. (b) Specific heat (black) in arbitrary units and normalized electrical resistance (red) for selected applied pressures. The black arrows indicate the superconducting transition ($T_c$) in the specific heat; $T_{S1} - T_{S3}$ indicate additional anomalies related to structural phase transitions. The red arrows mark the onset of the resistive transition. The insets show details of the specific heat on a different scale. The data at 1 kbar were measured just after closing the cell. For technical reasons all following measurements at higher pressure have been made upon releasing the pressure starting from 24 kbar.
related to the superconducting transition. However, compared to the phonon background the large magnitude of the anomaly and the peak-like first-order nature of the transition indicate that its origin is not solely from superconducting degrees of freedom. At the same pressure a pronounced decrease in the residual resistivity (see figure 3) is observed, hence it is most likely that a structural transition approaches the superconducting state at this pressure, causing the peak-like anomaly. The true superconducting specific-heat transition is rather the step-like second order anomaly at 5.7 K which resembles a Bardeen–Cooper–Schrieffer (BCS)-like superconducting transition. The structural transition may be associated with strain which causes superconducting precursors above the true bulk superconducting transition temperature. A similar peak-like anomaly has been observed in BaFe$_2$As$_2$ in the specific heat under a pressure for which it is known that a structural/magnetic transition meets the superconducting transition line [34]. In the pressure range between 3 and 5 kbar several structural phase transition lines merge and may approach zero temperature in this pressure range [35]. In 11 kbar the magnitude of the anomaly decreases and splits into three distinct bumps at 8, 19 and 12 K. The BCS-like $T_c$ anomaly is still found at 6 K but the size of the jump is smaller than at lower pressures, which indicates that superconductivity is weakened in this pressure range. In only slightly higher pressure (12 kbar) a further broad upward step-like anomaly occurs at 12 K. At higher pressure no more signs of a superconducting transition and no further anomalies are observed. In figure 3, we summarize the data in the form of a low-temperature phase diagram of Ca122 under pressure.

Superconducting correlations occur below 12 K over a rather large pressure range from 1 to 16 kbar, which is consistent with phase diagrams in the literature based on resistivity data [19, 26]. A small specific-heat anomaly at $T_c$ is already observed in 1 kbar pressure and a large

Figure 3. Temperature versus pressure phase diagram of CaFe$_2$As$_2$ derived from our data. Squares: bulk superconducting transition temperature $T_c$ as obtained from the specific heat. Open circles: onset of the resistively determined superconducting transition. The triangles and diamonds represent specific-heat anomalies of structural phase transitions. Stars: 15 K resistivity values (plotted against the right-hand axis). Inset: normalized jump size of the superconducting anomaly in the specific heat which is closely related to the superconducting condensation energy.
anomaly is found between 7 and 12 kbar. The size of the specific-heat anomaly $\Delta C$ (see the inset of figure 3) is closely related to the superconducting condensation energy [28, 36] and a large anomaly indicates that the majority of the volume of the sample is in the superconducting state (compared to other 122 compounds, which superconduct at ambient pressure, we estimate that at least 50% of the volume becomes superconducting).

In most of the proposed phase diagrams in the literature it appears as if the two structural transition lines related to the transition from the T to O phase and from the T to cT phase do not approach low temperatures [15, 26]. The pronounced additional anomalies in the specific heat occur, however, in the pressure range where these two transition lines meet and indeed a pressure-induced transition from the O to cT phase must occur at low temperatures. This was confirmed by Goldman et al [35]: the transition line into the high-pressure cT phase drops to zero temperature at $\sim 4$ kbar pressure upon increasing the pressure and separates the magnetic low-pressure O phase from the high-pressure cT phase. Most likely, the anomalies we observe are related to this transition line. This pressure-induced structural transition causes a significant drop in resistivity at 15 K towards higher pressure at a pressure of $\sim 5$ kbar, which is also present in our data. A dramatic increase in size of the superconducting specific-heat anomaly occurs close to 7 kbar, which is certainly related to this pressure-induced structural phase change. This is further confirmed by the fact that the resistivity starts decreasing at the onset of this structural specific-heat anomaly. The absence of the cT transition upon releasing pressure [35] has been discussed with the possibility of having a strain-induced mixed phase of the O and cT phases located around this transition line. We cannot provide a clear statement from our data, but the fact that the structural transition anomaly splits into three distinct anomalies at 11 kbar may indeed be a sign that different crystallographic phases coexist within a certain pressure range.

To summarize, our specific-heat data measured in a Bridgman-type pressure cell allow us, based on a true bulk thermodynamic quantity, to conclude that pressure-induced superconductivity in Ca122 is certainly not a filamentary superconductivity originating from structural domain boundaries, but is a bulk property. Although we cannot rule out that a phase separation of different coexisting crystallographic phases may exist, we can estimate that at least 50% of the volume becomes superconducting. The bulk superconducting transition remains at temperatures below 7 K, whereas the onset of the broad resistive transition remains robust at 12 K. This demonstrates the need to use a bulk thermodynamic method for the exact determination of superconducting transition temperatures of iron pnictides superconductors, especially under the influence of pressure. A pronounced structural anomaly occurs in the pressure range from $\sim 7$ to 12 kbar, which we attribute to a pressure-induced transition from the low-pressure O phase to the high-pressure cT phase, which is approaching the superconducting phase. It runs over a certain pressure range (9 and 12 kbar) parallel to the superconducting transition line before it levels off towards higher temperature. The onset of this structural transition falls together with the onset of the resistive superconducting transition, indicating that strain-induced superconducting precursors may exist well above the bulk specific-heat transition and cause the strong discrepancy between the resistive and thermodynamic determination of the superconducting transition temperature.

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References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. 130 3296
[2] Norman M R 2008 Physics 1 21
[3] Kurmaev E Z, McLeod J A, Buling A, Skorikov N A, Moewes A, Neumann M, Korotin M A, Izyumov Yu A, Ni N and Canfield P C 2009 Phys. Rev. B 80 054508
[4] Zhao J, Adroja D T, Yao D-X, Bewley R, Li S, Wang X F, Wu G, Chen X H, Hu J and Dai P 2009 Nature Phys. 5 555
[5] Andersen O K and Boeri L 2011 Ann. Phys., Berl. 523 8
[6] Mazin I I and Schmalian J 2009 Physica C 469 614
[7] Chen X H et al 2008 Phys. Rev. Lett. 100 247002
[8] Rotter M, Tegel M and Johrendt D 2008 Phys. Rev. Lett. 101 107006
[9] Sasmal K, Lv B, Lorenz B, Guloy A M, Chen F, Xue Y Y and Chu C W 2008 Phys. Rev. Lett. 101 107007
[10] Zhao K, Liu Q Q, Wang X C, Deng Z, Lv Y X, Zhu J L, Li F Y and Jin C Q 2010 J. Phys.: Condens. Matter 22 222203
[11] Lv B, Deng L Z, Gooch M, Wei F Y, Sun Y Y, Meen J, Xue Y Y, Lorenz B and Chu C W 2011 Proc. Natl Acad. Sci. USA 108 15705
[12] Saha S R, Butch N P, Drye T, Magill J, Ziemak S, Kirshenbaum K, Zavalij P Y, Lynn J W and Paglione J 2012 Phys. Rev. B 85 024525
[13] Sefat A S, Jin R, McGuire M A, Sales B C, Singh D J and Mandrus D 2008 Phys. Rev. Lett. 101 117004
[14] Ren Z, Tao Q, Jiang S, Feng C, Wang C, Dai J, Cao G and Xu Z 2009 Phys. Rev. Lett. 102 137002
[15] Torikachvili M S, Bud’ko S L, Ni N and Canfield P C 2008 Phys. Rev. Lett. 101 057006
[16] Chu C W and Lorenz B 2009 Physica C 469 385
[17] Saha S R, Butch N P, Kirshenbaum K, Paglione J F and Zavalij P Y 2009 Phys. Rev. Lett. 103 037005
[18] Park T, Park E, Lee H, Klimczuk T, Bauer E D, Ronning F and Thompson J D 2008 J. Phys.: Condens. Matter 20 222204
[19] Kreyssig A et al 2008 Phys. Rev. B 78 184517
[20] Yildirim T 2009 Phys. Rev. Lett. 102 037003
[21] Tompsett D A and Lonzarich G G 2010 Physica B 405 2440
[22] Kasinathan D, Ormeci A, Koch K, Burkhardt U, Schnelle W, Leithe-Jasper A and Rosner H 2009 New J. Phys. 11 025023
[23] Tomic M, Valenti R and Jeschke H O 2012 Phys. Rev. B 85 094105
[24] Yu W, Aczel A A, Williams T J, Bud’ko S L, Ni N, Canfield P C and Luke G M 2009 Phys. Rev. B 79 020511
[25] Prokeš K, Kreyssig A, Ouladdiaf B, Pratt D K, Ni N, Bud’ko S L, Canfield P C, McQueeney R J, Argyriou D N and Goldman A I 2010 Phys. Rev. B 81 180506
[26] Lee H, Park E, Park T, Ronning F, Bauer E D and Thompson J D 2009 Phys. Rev. B 80 024519
[27] Lortz R, Tomita T, Wang Y, Junod A, Schilling J S, Masui T and Tajima S 2006 Physica C 434 194
[28] Lortz R, Junod A, Jaccard D, Wang Y, Tajima S and Masui T 2005 J. Phys.: Condens. Matter 17 4135
[29] Duncan W J, Welzel O P, Harrison C, Wang X F, Chen X H, Grosche F M and Niklowitz P G 2010 J. Phys.: Condens. Matter 22 052201
[30] Thomasson J, Ayache C, Spain I L and Villedieu M 1990 J. Appl. Phys. 68 5933
[31] Deemyad S 2004 PhD Thesis Washington University, St. Louis
[32] Bireckhoven B and Wittig J 1988 J. Phys. E: Sci. Instrum. 21 841
[33] Sullivan P F and Seidel G 1968 Phys. Rev. 173 679
[34] Lortz R et al unpublished
[35] Goldman A I et al 2009 Phys. Rev. B 79 26024513
[36] Wang Y, Lortz R, Paderno Y, Filippov V, Abe S, Tutsch U and Junod A 2005 Phys. Rev. B 72 024548

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