Spatially-resolved study of the Meissner effect in superconductors using NV-centers-in-diamond optical magnetometry

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Abstract
Non-invasive magnetic field sensing using optically-detected magnetic resonance of nitrogen-vacancy centers in diamond was used to study spatial distribution of the magnetic induction upon penetration and expulsion of weak magnetic fields in several representative superconductors. Vector magnetic fields were measured on the surface of conventional, elemental Pb and Nb, and compound LnNi2B2C and unconventional iron-based superconductors Ba1−xKxFe2As2 (x = 0.34 optimal hole doping), Ba(Fe1−xCo)xAs2 (x = 0.07 optimal electron doping), and stoichiometric CaKFe4As4, using variable-temperature confocal system with diffraction-limited spatial resolution. Magnetic induction profiles across the crystal edges were measured in zero-field-cooled and field-cooled conditions. While all superconductors show nearly perfect screening of magnetic fields applied after cooling to temperatures well below the superconducting transition, Tc, a range of very different behaviors was observed for Meissner expulsion upon cooling in static magnetic field from above Tc. Substantial conventional Meissner expulsion is found in LnNi2B2C, paramagnetic Meissner effect is found in Nb, and virtually no expulsion is observed in iron-based superconductors. In all cases, good correlation with macroscopic measurements of total magnetic moment is found.

1 Introduction

1.1. Meissner effect in superconductors
Contrary to simplified introductions into the subject of superconductivity, the expulsion of weak magnetic fields from a superconductor, known as the ‘Meissner–Ochsenfeld effect’ or more often just as ‘Meissner effect’, is still not fully explored both experimentally and theoretically when real samples of finite size are used. It is well established that weak magnetic field (less than the first critical field, Hc1, at the surface), penetrates a homogeneous superconducting ellipsoid shaped sample only to a small London penetration depth, λ. This sets the quantitative measure of a total diamagnetic moment, 4πM = V / (1 − N) (λ/R tanh R / λ − 1) which corresponds to a nearly complete flux shielding. Here V is the sample volume and N is the demagnetization factor and R is effective sample size [1]. However, the distinct characteristic property of a superconductor is the Meissner expulsion of a magnetic flux upon cooling through the superconducting transition temperature, Tc. Experimentally, measurements of the total magnetic moment upon cooling range from a (very rare) complete flux expulsion in clean and properly shaped type-I superconductors [2], to substantial expulsion in pinning-free conventional type-II superconductors [3–5], to practically no expulsion in iron pnictides [6], and even to magnetic moment enhancement. The latter effect known as paramagnetic Meissner effect [7–11] is observed in various materials with extreme sensitivity to disorder.

This variety of behavior is illustrated in figure 1 where total magnetic moment of macroscopic (mm-sized) superconducting samples was measured using Quantum Design magnetic property measurement system (MPMS). The results for a ‘perfect’ sphere of type-I Pb superconductor are a textbook example of a complete
Meissner expulsion, similar to previously published in [12, 13]. All samples were chemically homogeneous well-characterized single crystals and partial 'superconducting volume fraction' due to poor quality or granularity can be excluded.

Since magnetic moment of the sample depends on measurement protocol, for our following discussion it is important to define terminology and abbreviations we use throughout the paper. Two protocols are those commonly used in bulk sample measurements: (1) \( \text{ZFC-W} \)— sample is cooled in zero field to low temperature, \( T < T_c \) and a specified magnetic field is applied. Then the measurements are taken on warming through \( T_c \). (2) \( \text{FC-C} \)— the measurements are taken while the sample is cooled in a constant magnetic field. These two modes were used for both DC magnetization and nitrogen-vacancy (NV) magnetometry [14] described below.

The other two modes were used for measuring profiles of the magnetic induction across the sample using NV sensing: (3) \( \text{ZFC} \)— sample was cooled in zero field down to base temperature, \( 4.2 \, \text{K} \), and a specified magnetic field was applied, then magnetic induction profiles were measured; (4) \( \text{FC} \)— sample was cooled in a constant magnetic field down to base temperature, \( 4.2 \, \text{K} \) and magnetic induction profiles were measured without changing the applied field. A visual representation of the measurement protocols on a generic H-T phase diagram of type-I and type-II superconductors is given in figure 1(a).

It is impossible to interpret the DC measurements of total magnetic moment upon cooling (\( \text{FC-C} \)) without knowing the spatial distribution of the vector magnetic induction, \( \mathbf{B}(r) \), throughout the sample. The magnetic moment is the integral of \( \mathbf{B}(r) \) over the sample volume, hence spatially-resolved measurements are needed. To the best of our knowledge, there are very few reports of direct visualization of one component of the magnetic induction during FC-C process using magneto-optical techniques [2, 13, 15]. In fact although there are many spatially resolved studies of the magnetic induction or even individual Abrikosov vortices [16, 17], only recently structure of the Meissner expulsion was studied in thin films of Nb using a non-invasive vector magnetometry technique [18], a similar approach used in our work. However, the focus in [18] was only on the magnetic field penetration upon zero-field-cooled. In contrast, this work is a comprehensive study of penetration as well as expulsion of weak magnetic fields in several representative superconductors, using the four measurement protocols described above.

**Figure 1.** (a) Measurement protocols: \( \text{ZFC-W} \) (blue solid line), \( \text{FC-C} \) (red solid line), \( \text{ZFC} \) (blue circle), \( \text{FC} \) (red circle) on a generic H-T phase diagram of a superconductor. (b)–(e) Temperature-dependent total magnetic moment measured using Quantum Design MPMS. Shown are \( \text{ZFC-W} \) and \( \text{FC-C} \) curves measured in (b) superconducting lead sphere and single crystals of (c) LuNi$_2$B$_2$C borocarbide (d) niobium and (e) Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ (\( x = 0.070 \) optimal doping) in magnetic fields similar to those used for NV sensing.
In most experiments, the sample is a flat slab with large demagnetization effects that make field distribution highly non-uniform. Therefore, in the ideal case the measurement should be non-invasive and performed on a well-characterized sample with well-defined sharp edges, as determined from electron microscopy. In addition, measurements should provide sufficient spatial resolution and be sensitive enough to detect weak magnetic field from a few vortices. Also, the sample has to be stationary because motion in a magnetic field may lead to effective field changes due field gradients in finite size solenoids used in the experiment.

In this report we use a novel non-invasive optical magnetometer that satisfies these restrictions to probe the structure of the Meissner effect in several superconductors and show how different the behavior is. In some cases, such as ‘paramagnetic’ Meissner effect (PME) in Nb, we confirm the theory suggested by Koshelev and Larkin that flux compression is the most likely scenario for the observed apparent paramagnetism [19]. In other, such as iron based superconductors, we simply confirm that flux expulsion is virtually absent on the scale of the whole sample [6], although the reasons for that are still unclear. And, indeed, we observe conventional Meissner expulsion in cases where it is expected, such as low pinning borocarbides.

### 1.2. Optical magnetometer based on NV centers in diamond

The NV center is a defect in the diamond lattice that consists of a nearest neighbor pair of a substitutional nitrogen atom and a lattice vacancy shown schematically in figure 2(a). With an additional acquired electron, NV center has a spin triplet, \( S = 1 \), ground state. (In this paper, we exclusively consider the negatively charged NV- centers and simply refer to them as the NV centers). When excited to a higher energy level (i.e., by a 532 nm green laser) from the \( m_S = 0 \) spin projection ground state, the relaxation back to \( m_S = 0 \) proceeds through spin-conserving cyclic transitions emitting red photons. However, if excited from \( m_S = \pm 1 \) levels, the NV center can also relax via the meta-stable (dark) states to \( m_S = 0 \) resulting in a reduced red fluorescence rate. This spin-dependent fluorescence allows for optical detection of the magnetic spin resonance (ODMR) by sweeping frequency of microwave radiation. When the frequency matches the energy difference between \( m_S = 0 \) and \( m_S = \pm 1 \) levels, i.e., when electron spin resonance (ESR) occurs, the fluorescence rate is minimal. In the presence of magnetic field, the frequency of ESR signal is shifted owing to the Zeeman effect, thus the change of resonance frequency can be used as a probe to accurately measure the local magnetic field. As a consequence of long coherence time, convenient energy levels spacing and several important advances in the measurement protocols, NV centers in diamond are now emerging as a promising candidate for non-invasive optical magnetometry with nano-scale spatial resolution [14, 20–24]. A detailed review of the NV-centers and NV magnetometry can be found in [14, 25]. The non-invasive nature of the technique is very important for probing delicate states, especially those where quantum coherence is important, where conventional measurements may alter the state of the studied system.

![Crystal structure of diamond with NV center and its energy levels.](image)

**Figure 2.** (a) Crystal structure of diamond with NV center and its energy levels. Under off-resonant 532 nm laser excitation, the NV center emits red photons. Due to the additional relaxation path via the meta-stable states the \( m_S = \pm 1 \) levels fluoresce less than \( m_S = 0 \) spin sublevel. (b) Experimental setup: a low temperature confocal fluorescence microscope optimized for NV detection. A thin diamond plate with NV centers formed on the bottom surface is attached in a configuration with the bottom (NV proximity) surface of the diamond plate in contact with the superconductor. The spatial resolution of the diamond sensor is determined by the convolution of the focal volume with the NV distribution in the diamond plate, leading to a disk-like probe of thickness \( \approx 20 \) nm and diameter \( \approx 500 \) nm.
The effective ground state Hamiltonian of an NV-center is given by:

\[ H_{\text{eff}} = DS_z^2 + E(S_x^2 - S_y^2) - \gamma_e \vec{S} \cdot \vec{B}, \]

where \( \gamma_e \approx 28 \text{ GHz} \cdot \text{T}^{-1} \) is the gyro-magnetic ratio of the NV electronic spin, \( D \approx 2.87 \text{ GHz} \) and \( E \approx 5 \text{ MHz} \) are axial and off-axial zero-field splitting parameters respectively [14]. In this work, we measure the magnetic fields through the detection of Zeeman splitting observed in the ODMR spectra. Although the axial zero-field splitting parameter exhibits some temperature dependence, \( dD/dT \approx -7.4 \text{ kHz K}^{-1} \) [26], magnetic field readout obtained via Zeeman splitting is unaffected.

The experimental apparatus incorporates a confocal microscope optimized for NV fluorescence detection. The fluorescence is stimulated by the green off-resonant 532 nm laser excitation and low-energy levels are populated by the microwave radiation applied using a single silver wire loop antenna coupled to a MW frequency generator. A thin diamond plate with an ensemble of NV centers embedded near the surface (~20 nm depth) is used as the magneto-optical sensor. The spatial resolution of the sensor is determined by the effective size of the probe, which is essentially a convolution of the focal volume with the NV distribution in the diamond plate. This leads to a disk-like probing volume of thickness \( \approx 20 \text{ nm} \) and diameter \( \approx 500 \text{ nm} \). See Methods for more details.

Figure 3(a) shows the ODMR spectrum for different values of the external magnetic field when there is no sample mounted in the experiment. For a single crystalline diamond plate with [100] surface placed normal to the field, all four NV orientations result in the same Zeeman splitting. See appendix for more details. The slight broadening of the ODMR resonances at higher magnetic fields is most likely due to a small mismatch in the normal direction of the crystalline plane with respect to the magnetic field. Moreover, the NV centers here always experience a perpendicular component of the magnetic field with respect to their N-V axis. This leads to level mixing at higher magnetic fields, resulting in lower contrast of the ODMR signal [27, 28] which limits the practically measurable fields to about 200 Oe. The sensor also loses its sensitivity when Zeeman splitting is comparable with the off-axis splitting parameter \( E \), leading to a lower-bound of approximately 2 Oe for the directly measurable fields [14, 18].

Figure 3. (a) ODMR spectrum of the sensor when there is no sample mounted, for several values of the external magnetic field. For a single crystalline diamond plate with [100] surface placed normal to the field, all four NV orientations result in the same Zeeman splitting. (b) Experimentally measured Zeeman splitting versus the applied magnetic field. The dashed line is the theoretically anticipated curve, 3.233 MHz/Oe (see appendix).
2. Methods

2.1. Sensor preparation
An electronic grade single crystalline diamond plate with [100] surface from Element Six was further thinned down and polished to 40 \( \mu \)m thickness by Delaware Diamond Knives, Inc. It was then subjected to 14 keV Nitrogen ion irradiation with \( 10^{15} \) cm\(^{-2} \) ion dose by Leonard Kroko, Inc. According to SRIM calculation, this leads to \( \approx 20 \) nm projected range of Nitrogen ions in diamond with a straggling of 6.5 nm. Nitrogen implanted diamond plates were then subjected to 20 keV energy electron irradiation in a scanning electron microscope (SEM). Consequently, the diamond plates were annealed under 800 °C in vacuum \((\sim 10^{-5} \) Torr\) for 2 h. This mobilizes the vacancies and forms NV centers [47–49]. Finally, the diamond sensor was subjected to several steps of cleaning including solvent cleaning, acid cleaning with HNO\(_3\) and HCl 1:3 mixture, and Oxygen plasma cleaning.

2.2. Experimental setup
The experimental setup is based on low temperature atomic force microscope combined with a confocal fluorescence microscope (Attocube AFM/CFM) in a ³He bath cryostat with a base temperature of 4.2 K. Higher temperatures are achieved via a resistive heater and a temperature controller (LakeShore335). Optical filters in confocal microscope optimize the NV detection. A low-temperature compatible dry microscope objective (Attocube LT-ASWDO 0.82 NA) is used in this confocal setup for NV excitation and collection of fluorescence emission. Phonon-mediated fluorescence emission \( (600–750 \) nm) of NV centers are detected under coherent optical excitation \( (Laserglow R531001FX 532 \) nm LASER\) using a single photon counting module \( (Excilitas SPCM-AQRH-14)\). The waist size \((\text{diameter})\) of the excitation laser focus spot is approximately 500 nm. The detection volume in a confocal geometry is roughly limited by the diffraction-limited waist size in the lateral dimension and Rayleigh-length in the longitudinal direction. However, because the NV distribution in diamond sensor is limited to \( \approx 20 \) nm depth, the effective probe size at any point of measurement could be approximated to a disk-like shape with \( \approx 500 \) nm diameter and \( \approx 20 \) nm thickness. Background static vertical magnetic field is provided by a NbTi superconducting magnet \( (Cryomagnetics 4G-100)\). Microwave \((\text{MW})\) field is generated by a MW synthesizer \( (Rohde\&Schwarz SMIQ03B)\), amplified by a 16 W amplifier \( (Minicircuits ZHL-16W-43+)\) and delivered to the NV sensor via a loop antenna formed by a 50 \( \mu \)m diameter silver wire held between the diamond sample and the microscope objective. A National Instruments DAQ card \( (NI PCIe 6323)\) is utilized for data acquisition.

3. Results and discussion

3.1. Single crystal Pb
We begin with single crystal Pb, a pure type-I superconductor. Figure 4 shows NV measurements on a disk-shaped Pb sample. The inset in panel (a) shows diamond slabs attached on top of the disk. Filled blue symbols in panel (a) show ODMR splitting measured on warming after a small magnetic field of 10 Oe was applied at 4.2 K to which the sample was cooled without field \( (ZFC-W)\). Open red circles show the measurements performed on cooling the sample from above \( T_c \) in the same field of 10 Oe \( (FC-C)\). To avoid complications related to demagnetization, ODMR was measured near the sample center \((\text{point ‘a’ in the inset})\). Blue solid curve shows the fitting for the ZFC data to a sigmoid function [29]:

\[
S(T) = \frac{a}{1 + \exp \left( \frac{T - T_c}{\delta T_c} \right)} + b,
\]

where \( a, b, T_c, \) and \( \delta T_c \) are fitting parameters, from which we obtain the critical temperature \( T_c = 7.2 \pm 0.1 \) K.

In particular, a complete Meissner expulsion was observed in Pb crystals both from the measurements of the total magnetic moment and from direct magneto-optical visualization of the magnetic induction, thanks to a large-scale \((\text{tens and hundreds of } \mu \text{m})\) depending on the conditions\) laminar flux structure as opposed to sub-\(\mu \text{m}\)-sized Abrikosov vortices [12, 13]. The laminar structure appears in the intermediate state in type-I superconducting samples with non-zero demagnetization factor upon flux exit, whereas a tubular structure appears upon flux entry. \((\text{This difference in flux topology is known as ‘topological hysteresis’}\) [2, 13]. The peak in FC-C curve just below \( T_c \) in figure 4(a) is most likely due to normal phase lamella crossing the measurement point [13]. Figure 4(b) shows FC profile across the sample edge along the path ‘b’ of the upper inset. As discussed in appendix, two different sets of the resonance splitting are related to normal and longitudinal components of the magnetic induction at the location of NV centers. Meissner expulsion is clearly observed inside the sample and some variation is due to normal lamina pinned inside.
3.2. LuNi$_2$B$_2$C

For comparison with type-I superconductors, we studied flux expulsion in a single crystal LuNi$_2$B$_2$C, a type-II superconductor with low vortex pinning strength [30, 31]. As before, filled blue symbols in figure 5(a) shows ODMR splitting measured on ZFC-W whereas open red circles show the FC-C measurements performed in the same field of 10 Oe. Sigmoid fit to the ZFC data (blue solid curve) results in a critical temperature $T_c = 16.6 \pm 0.1$ K, which is consistent with the literature [30].

Magnetic induction (FC) profile across the sample after cooling in a 100 Oe magnetic field from above $T_c$ to 4.2 K is shown in figure 5(b). This profoundly non-monotonic spatial distribution was previously observed in magneto-optical experiments with bismuth-doped iron garnet indicators in clean Y–Ba–Cu–O crystals [32]. This dome-like shape is induced by the competition between temperature-dependent critical current and temperature-dependent London penetration depth. As expected Meissner currents are significant only near the edges and the corresponding diamagnetic susceptibility, $4\pi\chi = V^{-1}\int_{\text{whole space}} (B/H - 1) dV$ in the whole space (inside and outside the sample) will be non-ideal. $H$ here is the applied field without demagnetization correction.

3.3. Single crystal Nb

An obvious choice of a conventional type-II superconductor would be niobium. However, this material is far from being conventional as far as its properties in a magnetic field are concerned. In addition to a well documented PME in low magnetic fields [9, 10] it also exhibits a significant increase of the upper critical field with disorder. The pinning strength in Nb is very sensitive to small perturbations and this may promote thermomagnetic instabilities and even lead to a catastrophic collapse of the critical state [33]. Figure 6 shows field-cooled flux profiles across a 5 mm diameter and 1 mm thick Nb disk for three values of the applied
magnetic field. The inset shows temperature-dependent signal measured at two locations, 'P' and 'V' corresponding to local maximum and local minimum as marked on the lower curve. Clearly, Nb does not exhibit a uniform Meissner expulsion upon field cooling, although at higher fields (50 Oe), the mean value is less than applied field implying negative total magnetic moment. For lower applied magnetic fields, an increase of the
local magnetic induction values is observed at many randomly appearing regions. The mean value of the induction is greater than the applied field and, therefore, total magnetic moment will be positive, phenomenon known as the PME [7–11, 34, 35]. This PME is directly seen in our figure 1(d). By repeating the experiment in the same and slightly different fields we observed that the structure of the magnetic induction modulation is not stochastic and is quite reproducible (see comparison of 10 and 12 Oe in figure 6). This implies that the PME in Nb is due to some spatial variation in $T_c$ and/or critical current density (as noted above, Nb shows very strong response to small amounts of disorder). This mechanism is also compatible with the idea of vortices finding spatially inhomogeneous metastable states that maximize total magnetic flux [11]. Such mesoscale-sized samples as studied in [11] can also be studied using our approach and we intend to continue these studies, perhaps with single-NV scanning nano-probes [20, 21]. Although a comprehensive study on PME is beyond the scope of this paper, we believe that inhomogeneous cooling and flux compression is the cause of PME observed in Nb as proposed theoretically by Koshelev, Larkin and Vinokur [10, 11, 19, 36]. For a detailed review on PME, we refer the reader to reference [37].

3.4. Iron pnictides

3.4.1. Optimally electron-doped $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)\text{As}_2$, $x = 0.070$

Iron based superconductors are of immense interest for their various unusual properties. A particular interest here is anomalous Meissner effect identified by our group in these materials from the measurements of total magnetization [6]. Specifically, virtually no expulsion is observed upon cooling in low magnetic fields and the amount of expelled flux increases linearly with the increase of the applied magnetic field. As discussed in the introduction, such measurements of total magnetic moment always leave room for possible artifacts (for example induced magnetic field variation due to mechanical motion of the sample during MPMS measurement). Therefore, such measurements should be ideally supported by the spatially-resolved techniques. Unfortunately, magneto-optical imaging is either not sensitive enough or there is truly no substantial Meissner expulsion in iron pnictides. First we study single crystal of $\text{Ba(Fe}_{1-x}\text{Co}_x)\text{As}_2$ at optimal doping $x = 0.07$. Iron pnictides are known for their often very layered morphology and we examine the samples in a SEM and choose one with well-defined rectangular shape and good surface and edge (figure 7(a)). The dimensions of the sample studied here are $\sim 1 \times 1.1 \times 0.06 \text{ mm}^3$.

The inset in figure 7(b) shows superconducting phase transition at $T_c \approx 24$ K measured near the sample center, consistent with previous measurements of the same composition [38]. Figure 7(b) compares FC (solid red circles) and ZFC (filled blue circles) Zeeman splitting profiles at 100 Oe (top) and 5 Oe (bottom) applied magnetic fields. As expected, the two Zeeman pairs were observed in the ZFC profiles near the edge due to change in direction of the net magnetic induction field, caused by the shielding currents. Importantly, the FC profiles show no Meissner expulsion at all. This is consistent with the global measurements reported for this system [6], but is very different from ordinary Meissner effect in LuNi$_2$B$_2$C or PME behavior in Nb shown above. There is no clear explanation for this effect, but we confirm its existence in spatially resolved measurements on a stationary sample.

3.4.2. Stoichiometric $\text{CaKFe}_4\text{As}_4$

To gain further insight and see if the disorder from chemical substitution is to blame for the observed anomalous Meissner effect, we turned to a most recent addition to the pnictides family, stoichiometric $\text{CaKFe}_4\text{As}_4$ [39]. The studied rectangular cross-section sample had dimensions of $\sim 1 \times 1 \times 0.01 \text{ mm}^3$. Inset in figure 8 shows the superconducting phase transition at the critical temperature $T_c = 35.3 \pm 0.8$ K, consistent with previous measurements [39]. Despite having lower chemical substitution disorder compared to doped iron pnictides, the FC profile is flat and shows no change after cooling below $T_c$.

3.4.3. Optimally hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, $x = 0.34$

The study of ‘122’ derived pnictide superconductors would not be complete without hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. Here we study the Meissner expulsion of $\sim 1.5 \times 1.4 \times 0.03 \text{ mm}^3$ sized rectangular optimally-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ sample with $x = 0.34$. The SEM images are shown in figure 9(a) and we chose the edge shown in the right panel for the measurements. Figure 9(b) shows superconducting phase transition at the critical temperature $T_c = 38.9 \pm 0.2$ K, consistent with previous measurements [40, 41]. Figure 9(c) compares the FC and ZFC flux profiles at 5, 20 and 100 Oe applied magnetic fields at 4.2 K. As in the previous cases, the FC curves show neither Meissner expulsion nor PME behavior.
4. Discussion

Traditionally, the FC-C behavior in type II superconductors could be explained as follows: when cooling from above $T_c$ in a magnetic field $H$, Abrikosov vortices are formed at $T_c (H)$ (or, equivalently, at $H = H_{c2}(T)$). In an ideal case of zero pinning Meissner expulsion is effective until the distance between vortices becomes of the order of London penetration depth, $\lambda$, because largest density Meissner currents that are flowing in the so-called ‘Meissner belt’ around the edges of a finite sample (also of width of the order of $\lambda$), push the vortices into the sample creating dome-like flux distribution \[42, 43\]. Therefore, the degree of the macroscopic flux expulsion will always be less than 100% and its value is determined by the complex competition between temperature.

Figure 7. (a) Scanning electron microscope (SEM) images show the measured Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ crystal at optimal doping $x = 0.070$ with a reasonably rectangular shape and smooth surface. (b) FC and ZFC profiles for applied magnetic field of 100 Oe (top) and 5 Oe (bottom) measured at 4.2 K. $x < 0 (>0)$ is outside (inside) the sample. Inset shows superconducting phase transition at $T_c \approx 24$ K.

Figure 8. 100 Oe FC and ZFC profiles at 4.2 K of CaKFe$_4$As$_4$. (inset) Detection of superconducting phase transition at $T_c = 35.3 \pm 0.8$ K.
dependent $\lambda(T)$ and $\zeta(T)$ as well as demagnetization effects that renormalize magnetic field at the edges depending on the amount of the expelled flux. Demagnetization, especially pronounced in commonly studied thin platelet samples in perpendicular magnetic field, leads to highly inhomogeneous distribution of the internal magnetic field making the process of flux expulsion very non-local. Adding temperature-dependent pinning further complicates the situation. In any case, virtual absence of flux expulsion anywhere across the sample is highly unusual and seems to be a unique feature of iron pnictides. We can speculate that in iron pnictides where no long range ordered vortex lattice is observed, disordered and entangled vortices are not able to move out easily and their motion is also complicated by the flux cutting. Furthermore, very small vortex core makes iron pnictides susceptible to any microscopic variation of the order parameter and/or mean free path due to compositional variations and/or iron magnetism. Perhaps, this is related to pair-breaking nature of non-magnetic disorder due to $s_\pm$ pairing of iron based superconductors. It must be noted that a small Meissner belt was observed through Bitter decoration upon field-cooling in isovalently doped BaFe$_2$(As$_{1-x}$P$_x$)$_2$ pnictides. However, no comparison with flux penetration was given and no analysis of forces acting on fine magnetic particles near the edge was provided. Notwithstanding these experimental uncertainties, it is known that BaFe$_2$(As$_{1-x}$P$_x$)$_2$ is much cleaner and this result may support the idea that the degree of vortex lattice disorder plays an important role in iron pnictides. A detailed microscopic understanding of vortex expulsion in iron pnictides is lacking and we hope that our measurements will provide motivation for such theoretical work.

It is clear the textbook statement that weak magnetic field is fully expelled from an ideal superconductor is only applicable for an infinite sample without demagnetization and boundaries. A finite specimen, even with

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**Figure 9.** (a) SEM images of two sides of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ $x = 0.34$ crystal. The right side is chosen for profiling. (b) ZFC-W measured at the sample center showing critical temperature $T_c = 38.9 \pm 0.2$ K. (c) Comparison of ZFC and FC splitting profiles under applied magnetic field of 5, 20 and 100 Oe (from bottom to top) measured at 4.2 K.
zero pinning, will always have residual magnetic induction after field cooling of the order of the lower critical field, $H_{c1}$. The absence of Meissner expulsion at low fields and its appearance and increase at much higher fields (in a linear in field fashion, see [6]) implies that the amount of expulsion is scaled roughly as $H H_{c1}(0)/H_{c2}(0)$, so for iron pnictides it is very small, because $H_{c1}(0)/H_{c2}(0) \sim 10^{-3} - 10^{-4}$. In the limit approaching type-I superconductors, $H_{c1}(0)/H_{c2}(0) \rightarrow 1$, a complete expulsion is expected and observed. Of course, there may be other factors affecting the behavior.

5. Conclusion

In conclusion, we developed low-temperature optical magnetometer based on ensembles of NV centers in diamond crystal for studies of vector magnetic induction distribution in superconducting materials. This technique was used to study magnetic flux distribution upon penetration and expulsion of the magnetic field in representative superconductors. We find that the hallmark of superconductivity, the Meissner effect, is very fragile and sensitive to specifics of the material. In particular, while all studied samples exhibit a robust superconducting screening upon flux penetration, flux expulsion ranges from a conventional textbook diamagnetism to no expulsion at all, to even paramagnetic Meissner effect. While the elucidation of particular mechanisms behind these observations requires further studies, we have shown that spatially-resolved information provides crucially important insight into the interpretation of the results. For example, we showed that unusual paramagnetic Meissner effect is accompanied by large random variations of local magnetic induction lending experimental support to a theoretical model of random flux squeezing and, perhaps, finding metastable states that maximize the total flux upon cooling.

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Appendix. Decoding the ODMR splittings

The diamond lattice consists of two inter-penetrating face centered cubic Bravais lattices, displaced along the body diagonal of the cubic cell by 1/4 of length of the diagonal. It can be regarded as a face centered cubic lattice with the two-point basis: $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Here, we assume unit lattice constant for simplicity. The NV center is a point defect in the diamond lattice which consists of a nearest-neighbor pair of a substitution nitrogen atom, and a lattice vacancy.

The four nearest neighbors centered around the lattice point $V_0 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ are: $V_1 = (0, 0, 0)$, $V_2 = (\frac{1}{2}, \frac{1}{2}, 0)$, $V_3 = (\frac{1}{2}, 0, \frac{1}{2})$, and $V_4 = (0, \frac{1}{2}, \frac{1}{2})$. The four possible NV orientations can therefore be calculated as:

$$\hat{d}_i = \frac{V_i - V_0}{|V_i - V_0|}, i = 1, \ldots, 4,$$

$$\hat{d}_1 = (-1, -1, -1)/\sqrt{3}$$
$$\hat{d}_2 = (1, 1, -1)/\sqrt{3}$$
$$\hat{d}_3 = (1, -1, 1)/\sqrt{3}$$
$$\hat{d}_4 = (-1, 1, 1)/\sqrt{3}.$$

The Zeeman splitting between the $S_z = \pm 1$ states of an NV is given by $2\gamma_e |\vec{B} \cdot \hat{d}|$, where $\gamma_e \approx 2.8 \text{ MHz/Oe}$ is the gyromagnetic ratio of the NV electronic spin. It is only the magnetic field component that is along the NV orientation lead to Zeeman splitting. Therefore, the possible splittings in NV ensemble of a single crystalline diamond is given by $2\gamma_e |\vec{B} \cdot \hat{d}|$.

Case I

For a single crystalline diamond plate with [100] surface placed normal to the field $\vec{B} = (0, 0, B_z)$, all the possible NV orientations result in the same splitting:
\[ Z = \frac{2 \pi B_z}{\sqrt{3}} \approx 3.233 \text{ MHz/Oe.} \] (5)

Case II

If the magnetic field has two components such that \( \vec{B} = (B_x, 0, B_z) \), the NV ensemble will result in two pairs of Zeeman splittings. In this case,

\[
Z_{\pm} = Z|B_z \pm B_x|,
\]

\[
\max[B_{x,\pm}] = \frac{Z_i + Z_s}{2Z},
\]

\[
\min[B_{x,\pm}] = \frac{Z_i - Z_s}{2Z}.
\] (6)

Here, \( Z_i \) (\( Z_s \)) refers to larger (smaller) Zeeman splitting.

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