In-plane angular dependence of superconducting gaps in FeSe probed by high-resolution specific heat measurements

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The influence of a rotating magnetic field (in the *ab* plane) on the density of states has been investigated in the superconducting state of the nematic FeSe superconductor using high sensitivity specific heat measurements. As expected for (quasi-)nodal superconductors, oscillations in the specific heat C associated with the Doppler energy shift of Cooper pairs with momenta close to the gap minima are observed. In the $T_c = 9$ K crystal, $C(\phi)$ displays a twofold symmetry at low temperature and low magnetic field confirming the nematic character of FeSe from thermodynamical measurements. As expected, a $\pi/2$ phase shift is observed for increasing temperatures (at $H = 1$ T) but our measurements suggest that the gap structure abruptly changes above $\approx$1 K in this sample. At low temperature, the maxima observed for $H||a$ axis at low H split into lobes at $\pm 45^\circ$ when the magnetic field is increased, which can be accounted for by assuming that the electron gap rapidly closes with field.

I. INTRODUCTION

FeSe is a particularly interesting iron-based superconductor, composed only of a c-axis stacking of FeSe layers without any charge reservoir. Despite its moderate critical temperature ($T_c \approx 9$ K) this compound can be seen as an "extremely" high T_c material, lying at the verge of a Bose Einstein Condensation, due to its very low carrier density [1]. The Fermi, superconducting gap and Zeeman energies (for fields on the order of the $T = 0$ upper critical field) are then on the same order of magnitude leading to an unprecedented superconducting state of highly-spin-polarized electrons (see Refs. [2–4] for extensive studies of the H-T phase diagram). Moreover, in contrast with other iron-based materials, FeSe does not order magnetically [5] but superconductivity here competes with an orbitally ordered nematic state [6–8], which breaks the C_4 lattice symmetry down to C_2 below $\approx$90 K. Angle-resolved photoemission spectroscopy studies evinced strongly renormalized electron and hole dispersions, with a very anisotropic spectral weight in the normal state [7,9].

Unraveling the superconducting gap structure is then crucial to the understanding of this intriguing superconductor. Nematic order is expected to couple the s and d wave harmonics of the associated superconducting order parameter (of $s + d$ symmetry) but the amplitudes of the s (Δ_s) and d (Δ_d) components of the gaps are highly sensitive to nematicity and intra and interband coupling [10]. As a consequence, accidental gap nodes (i.e., for angles which do not correspond to high-symmetry directions of the crystal) can appear if $\Delta_d > \Delta_s$. It has finally been suggested that a transition from the $s + d$ to an $s + e^{i\alpha} d$ state could occur at low temperature for a (limited) range of s and d pairing interactions [10,11].

However, even if it is now well established that the gaps present a twofold anisotropy with pronounced minima along k_x and k_y for the electrons and holes, respectively [12–18], the temperature and field dependence of the gaps remains an open question. In particular, the presence of nodes remains controversial. Indeed, a nodal gap structure was inferred from both specific heat (see, for instance, the discussion in Ref. [16] and references therein) and scanning tunneling spectroscopy [1] measurements whereas nodeless superconductivity was rather supported by other specific heat [18] and thermal conductivity measurements [19,20]. Photoemission measurements [21] finally showed that the gap of the hole pocket has a finite minimal value in multidomain samples but gap values steeply dropping to zero in a narrow angle range in single-domain samples.

Specific heat C measurements in presence of a rotating in-plane magnetic field can then be an efficient mean in order to probe the gap structure of nodal—or highly anisotropic—superconductors. Indeed, in the mixed state, the flow of the Cooper pairs associated with the screening of the field in the vortex cores, locally shifts the energy required to create unpaired quasiparticles (the so-called Doppler shift). Rotating the magnetic field is then expected to lead to maxima (or minima) in the density of states [22], when $\delta E_{\mathrm{Dop}} \propto \vec{v}_s \cdot \vec{k}_F$ becomes on the order of the superconducting gap ($\vec{v}_s$ being the velocity of the screening currents). This (semiclassical) approach confirmed the oscillations previously inferred for intermediate magnetic fields within the so-called Brandt-Pesch-Tewordt approximation, taking into account the (spin-flip) scattering of the quasiparticles on vortices [23]. However, the amplitude of the $C/T(\phi)$ modulations are $\approx \gamma/100$ at best (γ being the Sommerfeld coefficient and ϕ

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the angle of the magnetic field within the *ab* pane), and a very high resolution is hence required to obtain fruitful information on the gap structure.

Modulations in $C/T(\phi)$ have been previously reported by Sun *et al.* [24] in a $T_c \approx 9$ K FeSe crystals confirming the strong anisotropy of the gaps, but no C_2 symmetry was observed in this preliminary work. Moreover, those modulations could only be observed in a limited T and H range ($H \lesssim 2$ T and $T \lesssim 2$ K) and could even not be observed at all in $T_c = 8$ K samples [25], indicating that the gap structure is very sensitive to the critical temperature (probably due to small changes in the Fe stoichiometry [26]). The aim of this paper is to present a more detailed study of those C/T oscillations using a very high sensitivity AC specific heat setup. We show in Sec. III that well-resolved oscillations can be observed up to 7 T and/or 6 K, in both $T_c = 8.1$ K and $T_c = 9.0$ K samples (hereafter labeled sample 1 and sample 2, respectively). The amplitude of the oscillations is nevertheless reduced by about one order of magnitude in the lower T_c sample (sample 1), confirming the strong sensitivity of the gap structure on minor changes in the sample [25].

Moreover, although qualitatively quite similar above ≈1.5 K, very different oscillation patterns are observed at lower temperatures. Indeed, whereas a C_4 symmetry is observed for all T and H values in sample 1 (but displaying 45° shifts with T and H, see discussion below), a clear C_2 symmetry is observed in sample 2 at low T and low H (see, for instance, data at $T = 0.5$ K and $H = 0.5$ T in Fig. 3 below). This C_2 symmetry unambiguously confirms the nematic character of FeSe from thermodynamical measurements. The C/T anisotropy then strongly depends on T and/or H and, in sample 2, the data can be very well reproduced by numerical calculations of the Doppler shift. Those calculations, however, reveal an intriguing T and H dependence of the gap structure which will be discussed in Sec. IV.

II. SAMPLES AND EXPERIMENTS

As indicated above, the preliminary measurements by Sun *et al.* [24,25] could not reveal the nematic character of FeSe, probably due to strong twinning of the sample. The size of nematic domains in FeSe is typically ranging from ≈10 to ≈100 μm in the absence of external strain [21]. Even if samples are (slightly) strained at low T in the C/T experiments discussed here due to the solidification of the grease, favoring single domains (slightly), miniature samples are still required to avoid twinning effects. Single crystals $\approx 10^{-2}$ mm^3 have hence been sorted out for this experiment [27] and we focus here on two of them. Those samples were synthesized by chemical vapor transport (see Refs. [13,16,28,29] for further information on the synthesis and first characterization) and present well resolved specific heat anomalies at $T_c = 8.1$ and 9.0 K in zero field, respectively, attesting for their good quality (see Fig. 1).

Besides their different T_c values, a striking difference between the two samples is the presence of a *second* C/T *anomaly* in sample 2 at $T^* \approx 1$ K [see Fig. 1(b)]. Similar 1 K anomalies ranging from smeared knees to well-defined bumps in C/T have been previously reported in several studies [14,16,17,25]. It is worth noting that the *jump* observed here

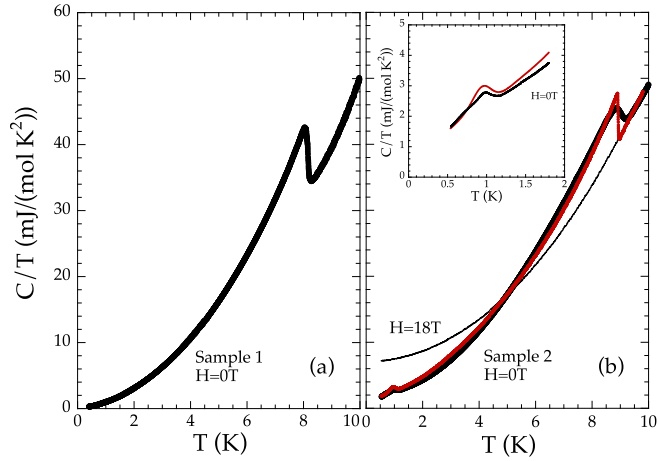

FIG. 1. Temperature dependence of the specific heat divided by the temperature in a FeSe single crystal for $H = 0$ (solid symbols) and $H = 18$ T [thin line in panel (b)]. As shown, a second anomaly is clearly visible around 1 K in sample 2. This anomaly is well reproduced by our calculations introducing the drastic change in the gap structure inferred from the in-plane anisotropy data (see red line and zoom in inset).

in sample 2 has been observed in most of the samples of the batch (but not all) and could even reach ≈4 mJ/(mol K^2) in some (rare) cases [27], clearly indicating that its presence or amplitude is very sensitive to minor changes from sample to sample. This 1 K anomaly has been initially attributed to the anisotropy of the gap structure in the $s + d$ wave model but this scenario cannot account for the existence of a *jump* in C/T (see discussion in Ref. [14]). It was then suggested that this anomaly could be attributed to the $s + e^{i\alpha}d$ transition mentioned above [11] but further theoretical works led to the conclusion that this scenario is unlikely as this transition only shows up in a narrow parameter range [10]. The origin of this 1 K anomaly hence remains an open question (see discussion in Sec. IV).

A very high resolution AC specific heat setup [27] (see also Ref. [4] for further details) has been used to study the angular dependence of C/T. We verified that no oscillations in C/T are present in the empty chip down to 0.5 K and up to 7 T, and checked for the good alignment of the samples within the *ab* plane [27]. Oscillations in the C/T anisotropy could then be resolved up to 6 K and/or 7 T in both samples (see Figs. 2–4 below). At 6 K, $\Delta C/C_{\rm tot} \approx 5 \times 10^{-4}$ ($C_{\rm tot}$ being the total specific heat including phonons and addenda) and the data for each angle have been averaged over approximatively 10 minutes to reach the required sensitivity ($\approx 5 \times 10^{-5}$).

III. IN-PLANE C/T ANISOTROPY

A. Experimental results

Figure 2 displays the temperature dependence of $C/T(\phi)$ for the two samples (at 1 T below 1.5 K and higher fields at high temperature). First note that, in contrast with earlier measurements [25], C/T modulations are observed in both samples despite their different T_c values. Nevertheless, the amplitude of the modulations is reduced by about one order of magnitude in the lower T_c sample (sample 1), confirming

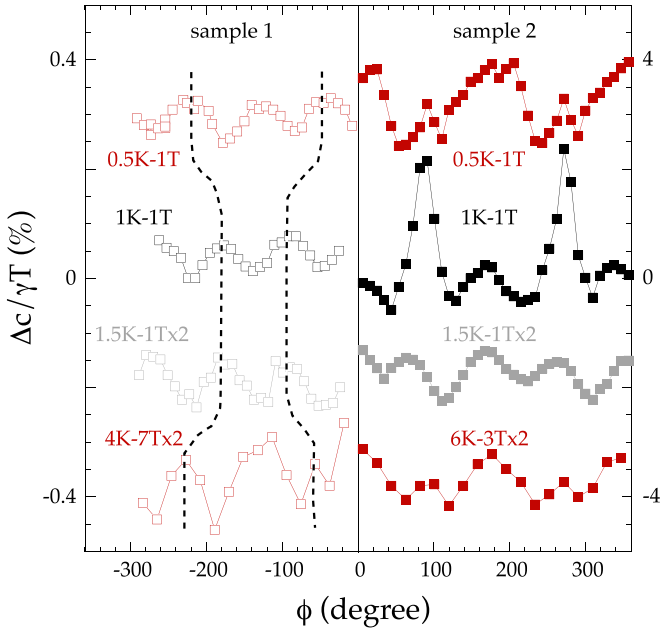

FIG. 2. Angular oscillations of the specific heat at $H = 1$ T for rotating magnetic fields within the *ab* plane in sample 1 (open symbols, left column) and sample 2 (closed symbols, right column) at the indicated temperatures (the different curves have been arbitrarily shifted for clarity). The $\phi = 0^\circ$ angle corresponds to the field aligned with the crystal edge i.e., the [100] direction of the low-T orthorhombic phase (as deduced from x-ray diffraction measurements on sample 1). As shown a C_2 symmetry is clearly visible in sample 2 confirming the nematic character of FeSe (note the dramatic fall of the modulation amplitude above 1 K, see also Fig. 3). The amplitude of the modulations is strongly reduced in sample 1 (of lower T_c) which only displays a C_4 symmetry. Dotted lines are guides to the eyes underlying the 45° phase shifts of the oscillations (see also Fig. 4 below and text for details). As shown oscillations could be observed up to high temperatures (and/or magnetic fields, see also Fig. 3) and two *inversions* of the oscillations are visible (red to black colors and dotted guides to the eyes).

[25] that the gap structure is very sensitive to the critical temperature. Even if iron stoichiometry much probably plays a significant role [26], the origin of this decrease of T_c remains unclear (it is worth noting that the superconducting transition is significantly sharper in sample 1 than in sample 2, despite its lower T_c value, ruling out a simple explanation in term of disorder). Whatever its origin, earlier works pointed out that this decrease is associated with a significant decrease of the gap maxima in lower T_c samples and suggested that nodes could be wiped out in those samples (see Ref. [12] and references therein). A less anisotropic gap structure is then expected to lead to smaller oscillations in $C/T(\phi)$, in qualitative agreement with our experimental data. However, as no C_2 symmetry could be observed in sample 1 (see Fig. 2), one could not exclude larger twinning in this latter sample and we did hence not perform any quantitative fitting of the data in this case.

On the contrary, the second striking feature is the clear C_2 symmetry observed at low T or low H in sample 2 (see Fig. 3 at 0.5 K or 0.5 T and additional data in the Supplemental Material [27]). This C_2 symmetry is unambiguously confirming the nematic properties of FeSe from thermodynamic measurements. Third, the maxima observed along $\theta = 0^\circ$ below ≈1 T progressively split into lobes at ±45° giving rise to a C_4 symmetry for $H \approx 4$ T (see bottom row of Fig. 3). Similarly, even if a C_4 symmetry was observed for all T and H in sample 1, a 45° shift of the pattern is observed for increasing H (see Fig. 4) or T [see dotted lines in Fig. 2(a)]. Finally, an abrupt change of the amplitude of the C/T anisotropy is observed around 1 K in sample 2 (see top row in Fig. 3 and additional data in Ref. [27]).

B. Numerical calculations

The C_2 symmetry observed in sample 2 at low T and low H clearly indicates that this miniature sample is only weakly twinned, allowing a detailed study of the T and H dependencies of the gap structure. For every set of temperature and magnetic field, we have hence performed numerical calculations of the $C/T(\phi)$ modulations in presence of the Doppler shift. The calculations are based on the model band structure used in Ref. [12], taking into account the orbital-dependent spectral weight and introducing the wave-vector dependent Doppler shift following the formalism of Graser [30], valid for small temperatures and magnetic fields (see the Supplemental Material [27] for details). The experimental $\Delta C/\gamma T$ curves have been fitted to the calculated ones after subtraction of the standard phonon and electronic contributions. As shown (see solid red lines in Fig. 3) a very reasonable quantitative agreement between calculations and experimental data can be obtained for all T and H values, by adjusting the hole and electron gap extrema. The minor discrepancies are much probably due to slight twinning, slight misalignment of the sample and/or "details" of the electronic structure.

As pointed out by Boyd *et al.* [22], the angular dependence of the specific heat oscillations at finite T and H does not merely reflect the low-energy density of states of the superconductor but involves the whole density of states up to the coherence peak energy. This can lead to an inversion of the maxima and minima of the specific heat depending on temperature and field, here well reproducing the 90° rotation of the C/T maxima observed around 0.75–1.0 K. Moreover, in the $s+d$ symmetry, accidental nodes can appear for $\cos(2\Psi) = -\Delta_s/\Delta_d$ (Ψ being the "renormalized" [10] angle along the Fermi pocket [31]). $C/T(\phi)$ then clearly differs from a simple $\cos(4\phi)$ function but the location of the maxima and minima cannot be directly anticipated and calculations based on the full band structure and gap functions are necessary. Those calculations here well reproduce the intriguing "butterfly" structure observed at $T = 0.75$ K (and $H = 1$ T, see top row in Fig. 3), clearly indicating the presence of accidental nodes in the gap structure, for both the electron and hole pockets. Note that modulation patterns very similar to those observed at low T/low$H$ are recovered at high T and high H (in both samples, see closed versus open symbols in Fig. 2). This *double inversion* is probably reminiscent of the one obtained by Vorontsov *et al.* [23] in the Brandt-Pesch-Tewordt approximation. Unfortunately the Doppler-shift approximation used in the numerical calculations presented below is only valid when vortices are far apart ($H \ll H_{c2}$) and for energies small

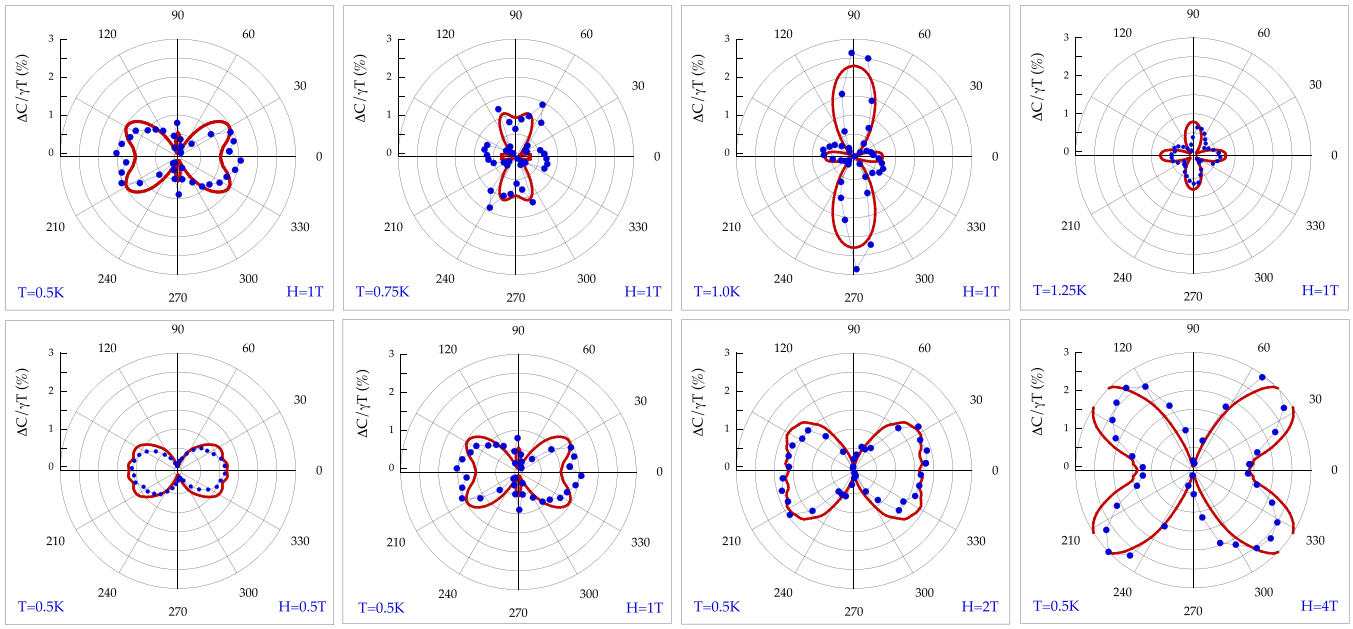

FIG. 3. Polar plot of the angular dependence of the specific heat (after subtraction of its minimal value) for rotating magnetic fields within the *ab* plane in FeSe (sample 2) at the indicated fields and temperatures (first row: temperature dependence at $H = 1$ T, second row: field dependence at $T = 0.5$ K). The solid red lines are numerical calculations of the $C(\phi)/T$ modulations in presence of the Doppler shift using the gap structure displayed in Fig. 4 and the electronic structure given in Ref. [12] (see Ref. [27] for additional data).

compared with the maximal superconducting gap, hindering calculations at high temperatures or magnetic fields.

The gap values deduced from this fitting procedure have been reported in Fig. 5. It is worth noting that the as-deduced low T, low H gap values are in very reasonable agreement with those previously obtained from (zero field) spectroscopic measurements [15] (see also discussion in Ref. [12]), hence supporting the validity of this fitting procedure. The presence of nodes in our (mainly) untwinned sample is also in good agreement with the conclusions previously drawn from angle-resolved photoemission measurements [21]. However, our measurements also suggest an intriguing T and H dependence of the gap structure, which will be discussed in the next section.

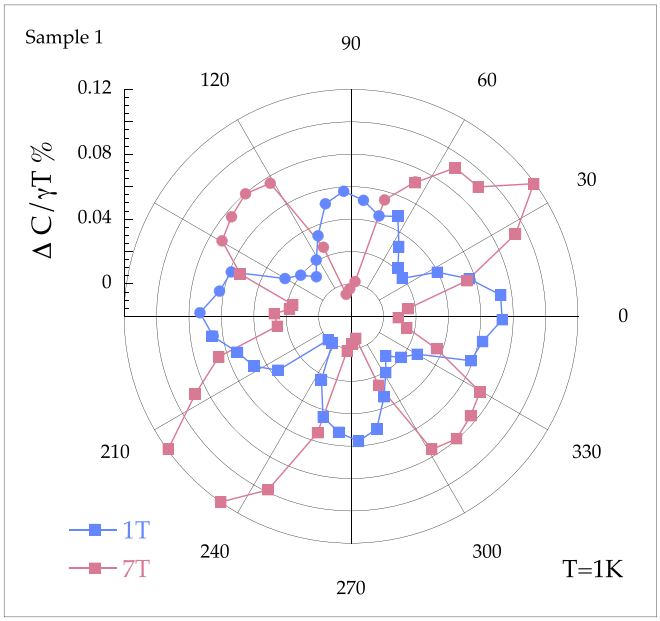

FIG. 4. Polar plot of the angular dependence of the specific heat (after subtraction of its minimal value) for rotating magnetic fields within the *ab* plane in sample 1 at 1 K and the indicated field values [solid circles correspond to data which were not directly measured but obtained by shifting the angles of the measured data (solid symbols) by 180°]. Note the 45° shift of the oscillation patterns between 1 and 7 T.

IV. DISCUSSION

A. Field dependence of the gaps (at low T)

Let us first discuss the influence of H. The lobes developing at ±45° in $C/T(\phi)$ when the magnetic field is increased at low temperature can be reproduced by assuming that the gap structure of the hole pocket only slightly depends on H [see Fig. 5(d) and Ref. [26] for additional data], but that both gap maxima and minima rapidly decreases with field for the electron pocket [see Fig. 5(b)]. It is worth noting that a qualitatively similar effect is observed in Sample 1 (see Fig. 4). Indeed, even if the absence of clear C_2 symmetry is hindering any quantitative analysis of the gaps (due to possible twinning), a clear 45° shift of the oscillation pattern is also observed in sample 1 when the magnetic field is increased at low T (a similar effect has also been reported in Ref. [23]). This shift cannot be attributed to the maxima or minima inversion expected from the Doppler-shift calculations [22] (around $H_{c2}/2$ i.e., ≈12 T in our case) because, even in the presence of twinning, this inversion would correspond to a 90° (and not 45°) shift for the nematic gap structure discussed here.

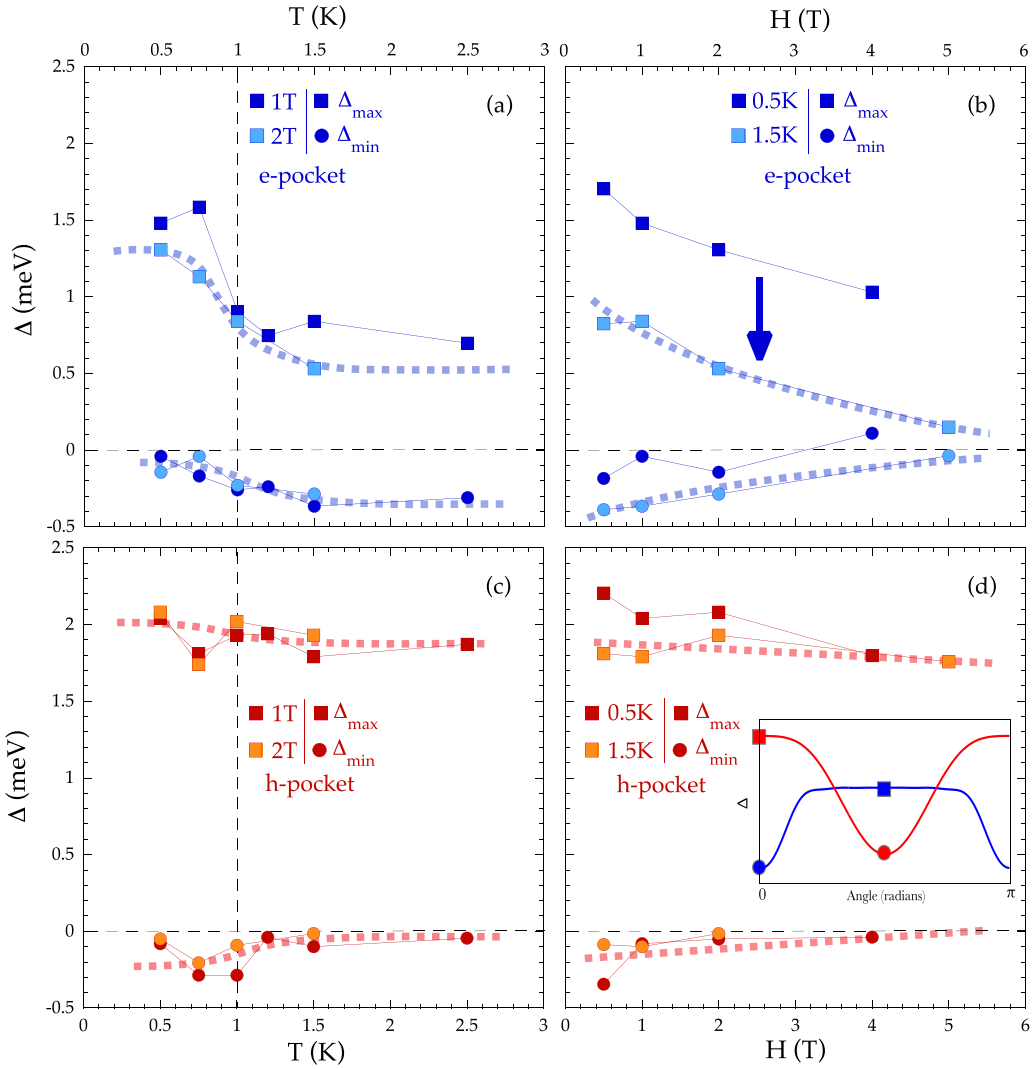

FIG. 5. (a), (c) Temperature [at $H = 1$ T (closed symbols) and 2 T (open symbols)] and (b), (d) field [at $T = 0.5$ K (closed symbols) and 1.5 K (open symbols)] dependence of the gap maxima (squares) and minima (circles) for the hole (red symbols) and electron (blue symbols) pockets of the Fermi surface, used to fit the angular dependence of the specific heat (solid red lines in Fig. 3). The inset of Fig. 4(d) displays the gap functions. As shown, a drastic change in the gap structure is observed for $T \approx 1.1$ K (see dashed guide to the eye at 2 T) for the electron pocket, where as the hole pocket remains almost temperature independent. For this electron pocket both Δ_{max} and Δ_{min} rapidly decrease with field (see dashed guide to the eye at 1.5 T) giving rise to lobes in the angular dependence of C/T (see Fig. 3). Note that this gap seems to vanish above ≈1.5 K or 5 T.

Furthermore, a rapid increase of the specific heat has been reported at low temperature below 2–3 T [16,24]. This increase is very similar to the one previously observed in MgB_2 due to the presence of both a robust σ gap (closing at H_{c2}) and a fast closing π-band gap, vanishing for magnetic fields $\approx H_{c2}/10$ [32]. This rapid increase of C/T in FeSe is then consistent with the closing of the electron gap (vanishing above ≈1.5 K or 5 T) in presence of a more robust hole gap. It has also been shown that the mixed state of FeSe also exhibits a vortex-lattice transformation from a nearly hexagonal to a nearly square lattice for magnetic fields between 1 and 4 T (applied along the c axis) which could result from the interplay between nematicity and the $s + d$ order parameter [33,34]. However, the influence of this interplay on the field dependence of the gaps still has to be clarified and to the best of our knowledge, there is no straightforward interpretation for the field dependence of the gaps deduced from $C/T(\phi)$.

B. T dependence of the gaps and 1 K anomaly

A shown in Fig. 2(a) (dotted line), in sample 1, a 45° shift is also observed when the temperature is increased from 0.5 to 1 K at 1 T, suggesting that the electron gap values also decrease with T. Likewise, a 45° shift is observed in sample 2 but for higher fields (see, for instance, data at 4 T in Ref. [27]) but, at 1 T, the temperature dependence is strikingly different in sample 2. Indeed, as shown in the bottom row of Fig. 3, a 90°—and not 45°—shift is observed in this case (in agreement with the minima and maxima inversion expected for $T \sim T_c/10 \approx 1$ K), followed by a *sudden* drop of the amplitude of the oscillations above ≈1 K. This decrease

can still be well reproduced by the numerical calculations, introducing however the temperature dependencies of the gap values displayed in Figs. 5(a)–5(c) (additional data in Ref. [26]). As shown, those calculations suggest that—as for H—the gap values of the hole band only weakly depends on T (with mainly a slight decrease of $\Delta_{\rm min}^{\rm hole}$). On the contrary, the electron gap maximum $\Delta_{\rm max}^{\rm electron}$ *abruptly* decreases from $\approx$1.5 meV to $\approx$0.7 meV above 1 K, and $\Delta_{\rm min}^{\rm electron}$ shift from $\approx$0 to ≈ -0.4 meV. Our measurements hence suggest that the symmetry of the electron gap becomes more "d like" above 1 K. As discussed in Ref. [10], this change would indicate that either the nematicity or the s or d coupling ratio of the electron band decreases above 1 K. Note that this d-like symmetry is preserved in field with both $\Delta_{\rm max}^{\rm electron}$ and $|\Delta_{\rm min}^{\rm electron}|$ decreasing with H [see Fig. 5(b)].

Strikingly this change in the gap values occurs in the close vicinity of the 1 K anomaly observed in the zero-field temperature dependence of C/T [see Fig. 1(b)] and concomitantly, no 1 K anomaly was observed in any of the samples of batch 1 for which the amplitude of the oscillations smoothly varies with T, remaining small down to the lowest temperatures. The origin of this 1 K anomaly in the temperature dependence of C/T is a long standing issue in FeSe. As discussed in Ref. [14], this anomaly cannot be attributed to the presence of Al precipitates ($T_c \approx 1.1$ K). Indeed, even if $AlCl_3$ salt has been used in the elaboration process (together with KCl), the affinity of aluminium is too high to be present as a metal (there is no reducing agent in the mixture). Moreover, no indication for aluminum could be detected in chemical analysis by energy dispersive x rays [35] (possible traces of $AlCl_3$ on the surface of crystals were washed off by water and ethanol prior to any measurement) and this 1 K anomaly is visible [27] up to $\approx$2 T (see also Ref. [14]), i.e., well above the critical field of Al ($\approx$0.01 T). This first scenario can hence be definitely excluded.

The magnetic state of FeSe remains a debated issue. In contrast with other iron-based materials no clear magnetic order has been observed in this system but strong spin fluctuations remain present. This system has been considered as a possible candidate for the existence of the long-sought quantum spin-liquid state [36,37] but a putative antiferromagnetic transition occurring at low T cannot be fully excluded [14]. An anisotropic (of C_2 symmetry) shift of the transition could then affect the amplitude of the C/T modulation in the vicinity of the transition, but this scenario still deserves further theoretical work to account for both this anisotropic shift (in relationship with nematicity) and the field dependence of the anomaly [14,27].

An alternative explanation would be that this anomaly is a *consequence* of the change in the electronic structure suggested by the numerical calculations. Indeed, the as-deduced T dependence of the gaps directly—and consistently—accounts for *both* the drastic change of in the in-plane specific heat anisotropy and the anomaly at 1 K. Indeed, k vectors contributions to the specific heat are proportional [27] to $[E_{\mathbf{k}}^2 + (\beta/2)(d\Delta_{\mathbf{k}}^2/d\beta)]$ (with $\beta = 1/k_BT$) and the $d\Delta^2/d\beta$ term then directly leads to a "jump" in C/T due to the rapid change of the gap structure around 1 T. This jump reproduces the 1 K anomaly observed in sample 2 in a very reasonable way [see red line in Fig. 1(b) and zoom on 0–2 K range in the inset] and this scenario hence provides a consistent explanation for all experimental observations without the need of introducing any additional feature. However, this scenario also requires further theoretical works to understand the origin of this *anomalous* T (and H) dependence of the electron gap (a change in the spin fluctuations or ordering in relationship with nematicity is most probably a promising path).

V. CONCLUSION

In summary, we have shown that the angular dependence of C/T of FeSe crystals for rotating magnetic fields within the ab plane can be reproduced very well by numerical calculations taking into account the Doppler shift. For samples of optimal T_c values ($\approx$9 K), our data confirm the nematic properties of FeSe from thermodynamic measurements and show that the gap structure clearly exhibits accidental nodes associated with the $s+d$ symmetry of the order parameter. While the gap of the hole pocket only weakly depends on T (and H), our data suggest a rapid change in the gap structure around $T \approx 1$ K for the electron pocket. This rapid change accounts for the 1 K anomaly observed in the temperature dependence of C/T in sample 2 (and reported in the literature in several cases). Moreover, the amplitude of both the gap maxima and minima of this pocket rapidly decrease with field, leading to an effective fourfold symmetry of the C/T modulations above $\approx$4 T at low temperature. The amplitude of the $C/T(\phi)$ modulations is decreased by about an order of magnitude in samples of lower T_c values, indicating that the gap structure is highly sensitive to T_c. The physical origin of this anomalous T and H dependencies of the gap structure remains to be explained but this interpretation falls beyond the scope of the present work.

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