

**Multigap superconductivity in single crystals of  $\text{Ba}_{0.65}\text{Na}_{0.35}\text{Fe}_2\text{As}_2$ : A calorimetric investigation**A. K. Pramanik,<sup>\*</sup> M. Abdel-Hafiez, S. Aswartham, A. U. B. Wolter, S. Wurmehl, V. Kataev, and B. Büchner  
*Institute for Solid State Research, IFW Dresden, D-01171 Dresden, Germany*

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We investigate the electronic properties and the superconducting gap characteristics of a single crystal of hole-doped 122 Fe-pnictide  $\text{Ba}_{0.65}\text{Na}_{0.35}\text{Fe}_2\text{As}_2$  by means of specific-heat measurements. The specific heat exhibits a pronounced anomaly around the superconducting transition temperature  $T_c = 29.4$  K and a small residual part at low temperature. In a magnetic field of 90 kOe, the transition is broadened and  $T_c$  is lowered insignificantly by an amount  $\sim 1.5$  K. We estimate a high electronic coefficient in the normal state with a value  $57.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ , being consistent with hole-doped 122 compounds. The temperature-dependent superconducting electronic specific heat cannot be described with single-gap BCS theory under the weak-coupling approach. Instead, our analysis implies a presence of two  $s$ -wave-like gaps with magnitudes  $\Delta_1(0)/k_B T_c = 1.06$  and  $\Delta_2(0)/k_B T_c = 2.08$  with respective weights of 48% and 52%. While our results have qualitative similarities with other hole-doped 122 materials, the gap's magnitude and their ratio are quite different.

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**I. INTRODUCTION**

The recent discovery of superconductivity (SC) in Fe-based pnictides<sup>1</sup> has lead to wide research activities in both experimental and theoretical frontiers of solid-state physics.<sup>2,3</sup> This is primarily because Fe-pnictides exhibit a high transition temperature  $T_c$ , a layered structure, and a proximity between magnetism and SC in their phase diagram, a scenario reminiscent of cuprates. However, Fe-pnictides are multiband metals where all five Fe-3d orbitals contribute to the electronic structure in the vicinity of the Fermi surface (FS), a stark contrast to cuprates, which are single-band Mott insulators. Detailed band structure calculations, indeed, show that the FS in Fe-pnictides is characterized by two electron-like cylinders around the  $M$  point and two hole-like cylinders plus a three-dimensional (3D) heavy hole-like pocket around the  $\Gamma$  point, therefore implying it is a possible multiband superconductor.<sup>4,5</sup>

As for superconductors in general, the central issue remains to understand the superconducting gap symmetry and the mechanism for Cooper pairing, which are still under debate in the case of Fe-pnictides. With a weak electron-phonon coupling in this class of materials,<sup>5–7</sup> theoretical calculations predict unconventional SC mediated by antiferromagnetic (AFM) spin fluctuations and an  $s_{\pm}$ -type superconducting gap symmetry where the order parameter requires a sign change between different sheets of the FS.<sup>5,8,9</sup> Experimental findings yet exhibit no consensus on the gap symmetry. For instance, nearly isotropic two full gaps with different magnitudes are evidenced in angle-resolved photoemission spectroscopy (ARPES) experiments for both electron- and hole-doped 122 Fe-pnictides.<sup>10–14</sup> A similar situation is observed in other studies, such as point contact Andreev reflection spectroscopy (PCARS)<sup>15</sup> and penetration-depth measurements.<sup>16–18</sup> On the other hand, the possible existence of nodes is revealed in the temperature  $T$  dependence of penetration-depth and nuclear magnetic resonance (NMR) measurements for both the 122 and 1111 series.<sup>19,20</sup> It can be mentioned that most of these investigations (except NMR) are surface sensitive; therefore, sample impurity or inhomogeneity at the surface may cause such contradicting results.

In this situation, specific heat  $C$  rather provides a key source of information regarding the bulk thermodynamic properties, exploring the electronic and gap structure in materials. In addition, it probes the system in equilibrium and low-energy states. Recent specific-heat studies in different families of Fe-pnictides have explored dissimilar gap properties with single to double gaps and even the presence of nodes, and this variation appears to be related to the nature as well as the level of doping.<sup>21–28</sup>

In this contribution we investigate the electronic properties and superconducting gap characteristics in a hole-doped 122 compound,  $\text{Ba}_{0.65}\text{Na}_{0.35}\text{Fe}_2\text{As}_2$  ( $T_c = 29.4$  K), by means of specific-heat measurements. Although such investigations have been performed in great detail for its K-doped analogues,  $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ , such studies are lacking in the Na-doped 122 family. It is, however, necessary to scrutinize how these properties are sensitive to different dopant species with unlike sizes and chemistry, considering the fact that the gap properties significantly modify with the nature of the doping elements. To be precise, ARPES experiments reveal that for hole-doped  $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ , the average gaps for the inner hole-like and two electron-like cylinders are similar, with a large value of  $\sim 12$  meV, while the outer hole cylinder has a lower value,  $\sim 6$  meV.<sup>10</sup> In contrast, for electron-doped  $\text{BaFe}_{1.85}\text{Co}_{0.15}\text{As}_2$ , the study shows that the inner hole pocket disappears, and average gaps of comparable sizes (6.6 and 5 meV) are observed in the outer hole and two electron cylinders.<sup>12</sup> These observations underline that detailed investigations are necessary in different compositional materials for a generalized understanding of these issues.

Our results show a pronounced specific-heat anomaly at  $T_c$  where the jump height is consistent with the  $T_c$  value according to recent results on Fe-pnictides. This transition is minimally suppressed in magnetic fields of 90 kOe. Our estimated electronic coefficient in the normal state is high, in agreement with other hole-doped 122 compounds. Our analysis further shows that the superconducting electronic specific heat cannot be described with the single-band weak-coupling BCS scheme; rather, it implies the presence of two  $s$ -wave-like gaps with different magnitudes and contributions. These results have

qualitative similarities to K-doped materials. However, the quantitative difference in the gap ratio may indicate the different density of states (DOS) in respective bands and the different interband interaction in these materials, hence highlighting the element-specific role of the dopant.

## II. EXPERIMENTAL DETAILS

Single crystals of  $\text{Ba}_{0.65}\text{Na}_{0.35}\text{Fe}_2\text{As}_2$  (BNFA) and  $\text{BaFe}_2\text{As}_2$  (BFA) used in the present study have been grown using a self-flux method. The details of sample preparation and characterization are described elsewhere.<sup>29,30</sup> The parent compound, i.e.,  $\text{BaFe}_2\text{As}_2$  has been used to estimate the lattice specific-heat contribution. The crystals have been characterized with x-ray diffraction (XRD), which implies the absence of any chemical impurity phase within the experimental accuracy. The mentioned chemical compositions of this material have been determined by energy dispersive x-ray analysis (EDX) spectroscopy performed at different locations on the sample. For the sample BNFA, the Na variation in the piece used is found within the instrumental error limit. A recent study on polycrystalline  $\text{Ba}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$  shows an unstable crystallographic phase in Na-rich compositions where the material is susceptible to chemical-impurity phases owing to the large mismatch in the size of  $\text{Ba}^{2+}$  and  $\text{Na}^{1+}$  ions.<sup>31</sup> In view of this, our results regarding the crystal homogeneity are remarkable. The BNFA crystal used in this study is about  $2.47 \times 1.98 \times 0.13 \text{ mm}^3$ . The magnetization  $M$  data have been collected using a SQUID-VSM (superconducting quantum interference device - vibrating sample magnetometer) made by Quantum Design. The heat capacity is measured along the crystallographic  $c$  axis with a physical property measurement system (Quantum Design) using a thermal relaxation technique down to 1.8 K and magnetic fields up to 90 kOe.

## III. RESULTS AND DISCUSSIONS

In Fig. 1(a) we present the temperature dependence of the volume susceptibility  $\chi_{\text{vol}}$  measured following the zero-field-cooled (ZFC) and field-cooled (FC) protocols for BNFA.  $\chi_{\text{vol}}$  has been deduced from the dc-magnetization data measured in

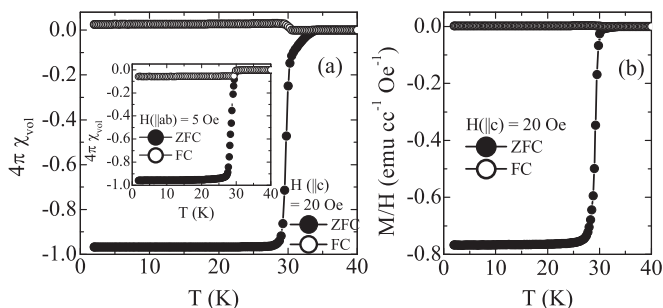


FIG. 1. (a) The volume susceptibility  $\chi_{\text{vol}}$  after demagnetization correction has been plotted as function of temperature. The  $\chi_{\text{vol}}$  has been deduced from the dc magnetization measured with  $H||c = 20$  Oe following ZFC and FC protocols for  $\text{Ba}_{0.65}\text{Na}_{0.35}\text{Fe}_2\text{As}_2$ . The inset shows the similarly deduced  $\chi_{\text{vol}}$  with  $H||ab$  plane ( $H = 5$  Oe). (b) The same data in the main panel of (a) have been plotted without demagnetization correction.

a field of 20 Oe applied parallel to the  $c$  axis. Care has been taken to correct the magnetization data for the demagnetization effect where the demagnetization factor has been estimated from an ellipsoidal approximation based on the dimensions of the crystal.<sup>32</sup> The material exhibits bulk SC, which is evident from the diamagnetic signal in the  $M_{\text{ZFC}}$  curve at low temperatures. Although the ZFC and FC magnetization already start to bifurcate around 34 K, our material shows a sharp superconducting transition (width  $\sim 1.5$  K) around 29.7 K determined from the inflection point in  $dM_{\text{ZFC}}/dT$ . However, similarly deduced  $\chi_{\text{vol}}$  with  $H||ab$  plane ( $H = 5$  Oe) shows a clear bifurcation between the ZFC and FC magnetization data around 29.5 K, as evident from the inset in Fig. 1(a). This difference in the onset of bifurcation between our ZFC and FC magnetization data for fields applied along different crystallographic directions will be studied in more detail in the future. Notably,  $\chi_{\text{vol}}$  exhibits an almost full diamagnetic shielding at low temperatures with fields parallel to both the  $c$  axis and  $ab$  plane. These results are in support of the good quality of our single crystal. The fact that  $M_{\text{FC}} > 0$  for  $H||c$  axis within the superconducting state seems to be an artifact in the data, probably arising from flux trapping during the FC process, which is likely for this field geometry due to layered structure in this material. Figure 1(b) shows the same data presented in main panel of Fig. 1(a) without demagnetization correction, demonstrating anomalies are not significantly evident. We would like to mention that the onset of negative magnetization at temperatures higher than the sharp transition in Fig. 1 with  $H||c$  axis is not visible in the specific-heat data, which exhibit a sharp jump around 29.4 K, as observed in the  $M_{\text{ZFC}}$  curve (shown below).

The temperature dependence of the specific heat in the form  $C/T$  vs  $T$  is shown in Fig. 2 for BFA in 0 Oe and for BNFA in 0 and 90 kOe. For our further analysis, the electronic contribution to the specific heat  $C_{\text{el}}$  is required for the material under study (BNFA). Since BNFA is nonmagnetic, the subtraction of the lattice specific heat  $C_{\text{ph}}$  from the total specific

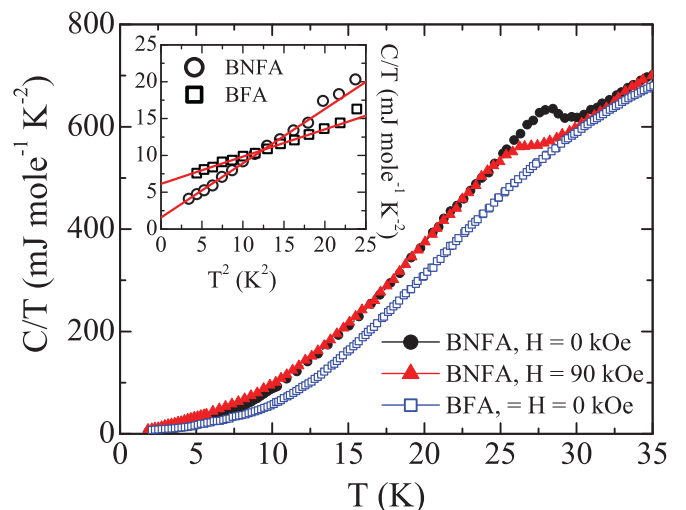


FIG. 2. (Color online) Temperature dependence of the specific heat  $C/T$  measured in 0 and 90 kOe for  $\text{Ba}_{0.65}\text{Na}_{0.35}\text{Fe}_2\text{As}_2$  and  $\text{BaFe}_2\text{As}_2$ . The inset shows  $C/T$  vs  $T^2$ . The straight lines represent linear fits to  $C/T = \gamma + \beta T^2$  (see text).

heat  $C_{\text{tot}}$  will simply serve our purpose. Conventionally,  $C_{\text{ph}}$  is estimated by suppressing the superconducting transition in high magnetic fields. However, the upper critical field  $H_{c2}$  is significantly high in this class of superconductors. Thus, we have estimated  $C_{\text{ph}}$  from its parent compound BFA, which is not superconducting throughout the temperature range, as evident from Fig. 2, where  $C/T$  does not exhibit any anomalous behavior as a function of temperature. On cooling from room temperature, BFA exhibits a long-range magnetic order of the AFM type paired with spin-density wave (SDW) formation around 140 K,<sup>33,34</sup> implying a likely magnetic contribution to its specific heat. In fact, our specific-heat data show a sharp peak around this AFM-SDW transition in BFA (not shown). However, a recent neutron-scattering measurement has revealed that the energy gap for low-energy spin-wave excitations in the magnetically ordered state is about 9.8 meV ( $\equiv 114$  K) for this material.<sup>35</sup> Therefore, magnetic contributions to the specific heat will be negligible in the range of our working temperatures ( $< 35$  K), and the specific heat can be assumed to consist of electronic and lattice contributions only.

The compound BNFA, on the other hand, shows an anomaly in  $C/T$  around 29.4 K (Fig. 2), which is marked by the superconducting transition. The temperature where this anomaly appears is consistent with the sharp superconducting transition in magnetization measurements (see Fig. 1). The jump in the specific heat is reasonably pronounced with a  $\Delta C/T_c$  value around  $84 \text{ mJ mol}^{-1} \text{ K}^{-2}$ , which is comparable to other hole (potassium) doped 122 compounds with a quantity around  $100 \text{ mJ mol}^{-1} \text{ K}^{-2}$ .<sup>22,24,36</sup> It is worth mentioning that the obtained  $\Delta C/T_c$  for the present material scales well with its  $T_c$  in light of recent results of Fe-pnictides.<sup>37</sup> The specific heat measured in a magnetic field of 90 kOe (Fig. 2) shows that the superconducting transition is broadened and insignificantly shifted ( $\sim 1.5$  K) in 90 kOe for BNFA, which is expected from its high  $H_{c2}$  estimated to be above 100 T.<sup>36,38</sup>

In the inset of Fig. 2, specific-heat data have been plotted in the form  $C/T$  vs  $T^2$  for the compounds BFA and BNFA. At low temperature, the data can be linearly fitted to  $C/T = \gamma + \beta T^2$ , where  $\gamma$  and  $\beta$  are the electronic and lattice coefficients of the specific heat, respectively.<sup>39</sup> For BFA, we obtain  $\gamma = 6.13(8) \text{ mJ mol}^{-1} \text{ K}^{-2}$  and  $\beta = 0.369(7) \text{ mJ mol}^{-1} \text{ K}^{-4}$ . From the obtained  $\beta$  value, we calculate the Debye temperature  $\theta_D$  following the relation  $\theta_D = [(12\pi^4 R n)/(5\beta)]^{1/3}$ , where  $R$  is the molar gas constant and  $n$  is the number of atoms per formula unit.<sup>39</sup> This gives  $\theta_D = 297$  K for BFA. The extracted value of  $\gamma$  in our crystal is consistent with other studies on single crystals of BFA ( $\sim 6.1 \text{ mJ mol}^{-1} \text{ K}^{-2}$ )<sup>40,41</sup> and close to theoretically predicted values, i.e.,  $5.68 \text{ mJ mol}^{-1} \text{ K}^{-2}$  (Ref. 42) or  $7.22 \text{ mJ mol}^{-1} \text{ K}^{-2}$  (Ref. 43). The fact that the specific-heat data  $C/T$  vs  $T^2$  for BNFA exhibit a linear behavior at low temperatures without any upturn discounts the possibility of Schottky-like contributions in our sample under study.

The phononic contribution  $C_{\text{ph}}$  to the specific heat of BFA has been determined following the relation  $C_{\text{ph}}^{\text{BFA}} = C_{\text{tot}}^{\text{BFA}} - C_{\text{el}}^{\text{BFA}}$ , where the  $C_{\text{el}}^{\text{BFA}}$  is  $\gamma^{\text{BFA}} T$ . We find that the specific heat is dominated by phonons in this region, i.e., around  $T_c$ ,  $C_{\text{el}}$  is only about 10% of  $C_{\text{ph}}$ . Using  $C_{\text{el}}^{\text{BNFA}}/T = C_{\text{tot}}^{\text{BNFA}}/T - f C_{\text{ph}}^{\text{BFA}}/T$ , we can calculate  $C_{\text{el}}^{\text{BNFA}}$ . The scaling factor  $f$  has

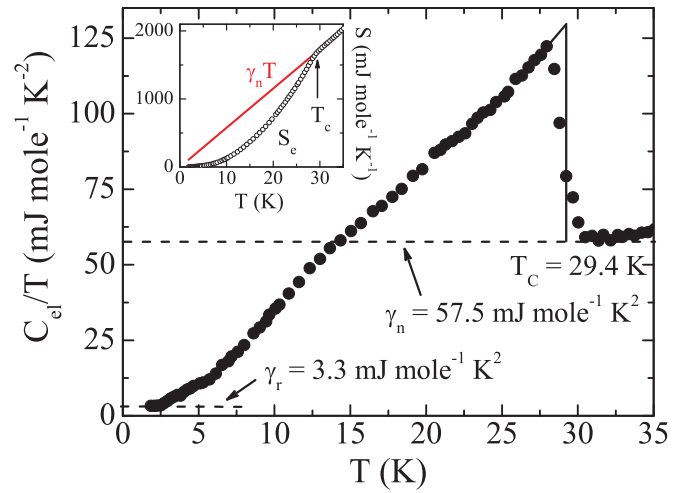


FIG. 3. (Color online) The electronic specific heat  $C_{\text{el}}/T$  as a function of temperature for the sample  $\text{Ba}_{0.65}\text{Na}_{0.35}\text{Fe}_2\text{As}_2$ .  $\gamma_n$  and  $\gamma_r$  represent the normal-state and residual electronic coefficients of the specific heat. The inset shows the entropy in the normal and superconducting states as a function of temperature.

been introduced due to slightly different atomic compositions between BNFA and BFA. To determine the value of  $f$ , we have used a criterion that normal- and superconducting-state entropies ( $S$ ) are equal at  $T_c$ , i.e.,  $\int_0^{T_c} (C_{\text{el}}/T) dT = \gamma_n T_c$ , where  $\gamma_n$  is the normal-state electronic specific-heat coefficient. We started with  $f = 1$ , but the entropy conservation criterion is satisfied for  $f = 0.95$  (inset in Fig. 3). This practice yields  $T_c = 29.4$  K. The resulting  $C_{\text{el}}/T$  for BNFA is presented in the main panel in Fig. 3. It is obvious from Fig. 3 that the superconducting transition at  $T_c$  is reasonably sharp, yielding a jump in  $C_{\text{el}}/T$  at  $T_c$  around  $72.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ . From our determined  $\gamma_n = 57.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ , we estimate the universal parameter  $C_{\text{el}}/\gamma_n T_c = 1.26$ . This value, however, is lower than the weak-coupling BCS prediction of 1.43.<sup>45</sup> Following the fact that the superconducting anomaly at  $T_c$  is reasonably sharp in BNFA, a distribution in  $T_c$  or the presence of an impurity phase is an unlikely explanation for such a reduced value of  $C_{\text{el}}/\gamma_n T_c$ . Instead, we believe that the presence of multiple SC gaps possibly render a low  $C_{\text{el}}/\gamma_n T_c$  in BNFA, as evidenced in other 122 Fe-pnictides.<sup>25,26,28</sup> Moreover, the signature of a multigap scenario in BNFA is evidenced by a significant hump around 12 K in our  $C_{\text{el}}/T$  vs  $T$  data (Fig. 3), which will be discussed below. Note that  $C_{\text{el}}/T$  almost saturates at low temperature; however, it does not extrapolate to zero, yielding a residual electronic specific-heat value  $\gamma_r = 3.3 \text{ mJ mol}^{-1} \text{ K}^{-2}$ . We mention that the presence of a finite  $\gamma_r$  is common in both electron- and hole-doped 122 crystals<sup>22–24,26,27</sup> and that the value of  $\gamma_r$  in our present case is remarkably low, showing the good quality of our single crystal. The origin of  $\gamma_r$  in BNFA is not clear; however, it may arise due to an incomplete transition to the superconducting state or broken pairs in the superconducting condensate.<sup>26,27,44</sup> Nonetheless, assuming a superconducting volume fraction  $(\gamma_n - \gamma_r)/\gamma_n \approx 95\%$ , our crystal consists of a high value, which is in fair agreement with our magnetization data (Fig. 1).

The obtained high value of  $\gamma_n$  for BNFA is consistent with other members in the hole-doped 122 series, whereas for

TABLE I. The superconducting transition temperature  $T_c$ , the jump height of the electronic specific heat  $\Delta C_{el}/T_c$ , the normal-state electronic specific-heat coefficient  $\gamma_n$ , and the superconducting gap properties  $\alpha_i$  and  $\gamma_i/\gamma_n$  extracted from specific-heat measurements for  $\text{Ba}_{0.65}\text{Na}_{0.35}\text{Fe}_2\text{As}_2$  along with other hole- and electron-doped 122 Fe-pnictides.  $\alpha_i$  and  $\gamma_i/\gamma_n$  represent the zero-temperature gap ratio and its weight in the  $i$ th band, respectively.

Compounds	Ref.	$T_c$ (K)	$\Delta C_{el}/T_c$ (mJ mol <sup>-1</sup> K <sup>-2</sup> )	$\gamma_n$ (mJ mol <sup>-1</sup> K <sup>-2</sup> )	$\alpha_i = \Delta_i(0)/k_B T_c, \gamma_i/\gamma_n$
$\text{Ba}_{0.65}\text{Na}_{0.35}\text{Fe}_2\text{As}_2^a$	This work	29.4	72.5	57.5	$\alpha_1 = 1.06, \gamma_1/\gamma_n = 0.48$ $\alpha_2 = 2.08, \gamma_2/\gamma_n = 0.52$
$\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2^a$	22	36.5	98.1	63.3	$\alpha_1 = 1.945, \gamma_1/\gamma_n = 1$
$\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2^b$	23	37.3	~100	49	$\alpha_1 = 2.07, \gamma_1/\gamma_n = 1$
$\text{Ba}_{0.68}\text{K}_{0.32}\text{Fe}_2\text{As}_2^a$	24	38.5	~120	50	$\alpha_1 = 1.1, \gamma_1/\gamma_n = 0.5$ $\alpha_2 = 3.3, \gamma_1/\gamma_n = 0.5$
$\text{KFe}_2\text{As}_2^b$	25	3.5	~21	69.1	$\alpha_1 = 0.3, \gamma_1/\gamma_n = 0.55$ $\alpha_2 = 2.4, \gamma_2/\gamma_n = 0.45$
$\text{Ba}(\text{Fe}_{0.925}\text{Co}_{0.075})_2\text{As}_2^a$	26, 27	21.4	30	23.8	$\alpha_1 = 0.95, \gamma_1/\gamma_n = 0.33$ $\alpha_2 = 2.2, \gamma_2/\gamma_n = 0.67$
$\text{Ba}(\text{Fe}_{0.92}\text{Co}_{0.08})_2\text{As}_2^a$	28	20	~22	18	$\alpha_1 = 0.957, \gamma_1/\gamma_n = 0.38$ $\alpha_2 = 2.175, \gamma_2/\gamma_n = 0.62$

<sup>a</sup>Single crystal.

<sup>b</sup>Polycrystal.

electron-doped 122 compounds  $\gamma_n$  is much lower (see Table I). Utilizing our value for  $\gamma_n$ , we can obtain information about the normal-state electronic properties, i.e., the DOS at the Fermi energy  $N(\epsilon_F)$  of BNFA, using the relation<sup>46</sup>

$$\gamma_n = \gamma_0 (1 + \lambda), \quad (1)$$

$$\gamma_0 = \frac{\pi^2 k_B^2}{3} N(\epsilon_F), \quad (2)$$

where  $\lambda$  is the electron-phonon coupling constant and  $k_B$  is the Boltzmann constant. Since in the case of Fe-pnictides  $\lambda$  is not significant, we can set  $\gamma_n \equiv \gamma_0$ . Therefore,  $\gamma_n$  is mainly contributed by  $N(\epsilon_F)$ , which implies a higher  $N(\epsilon_F)$  in hole-doped compounds than in electron-doped ones. From our  $\gamma_n$ , we calculate  $N(\epsilon_F) = 24.37$  states eV<sup>-1</sup> f.u.<sup>-1</sup>. It is worth mentioning that the generally high values of  $\gamma_n$  or  $N(\epsilon_F)$  for hole-doped 122 Fe-pnictides remains controversial, with theoretical calculations yielding  $\gamma_n = 13.03$  mJ mol<sup>-1</sup> K<sup>-2</sup> and  $N(\epsilon_F) = 5.526$  states eV<sup>-1</sup> f.u.<sup>-1</sup> for  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$ , where the related values are only around 20% higher than the parent compound.<sup>47</sup> However, another calculation clarifies that upon including the band parameters from experimental ARPES data as well as mass renormalization effects, the calculated  $\gamma_n$  is close to the experimental values.<sup>48</sup> Nonetheless, this controversy calls for further rigorous theoretical investigations adopting possible reconciliations within the experimental findings.

After exploring the electronic specific heat and electronic structure, we now examine the superconducting gap properties in BNFA. In many cases, specific-heat measurements have already been proved to be an effective tool in understanding the superconducting gap structure and its distributions.<sup>49,50</sup> For our sample, however,  $C_{el}$  first needs to be corrected due to a finite  $\gamma_r$ . At low temperature  $C_{el}$  is assumed to be contributed by the superconducting ( $C_{el-s}$ ) as well as the nonsuperconducting normal ( $C_n$ ) parts of the specific heat. While the normal electrons will have specific-heat

contributions linear in temperature ( $\gamma_r T$ ), the superconducting electronic contribution will be scaled by  $1 - \gamma_r/\gamma_n$ . On this basis, the sum of the individual contributions to  $C_{el}$  allows us to extract  $C_{el-s}$  from the following relation:

$$C_{el-s}/T = \frac{\gamma_n}{\gamma_n - \gamma_r} (C_{el}/T - \gamma_r). \quad (3)$$

In Fig. 4 we present the normalized data  $C_{el-s}/\gamma_n T$  as a function of reduced temperature  $t (= T/T_c)$  for BNFA. As mentioned earlier,  $C_{el-s}/\gamma_n T$  exhibits a broad hump around  $t = 0.4$ , which implies the presence of multiple SC gaps in this compound. We have analyzed our specific-heat data utilizing the  $\alpha$  model, which was originally proposed to account for the thermodynamic properties of a strongly

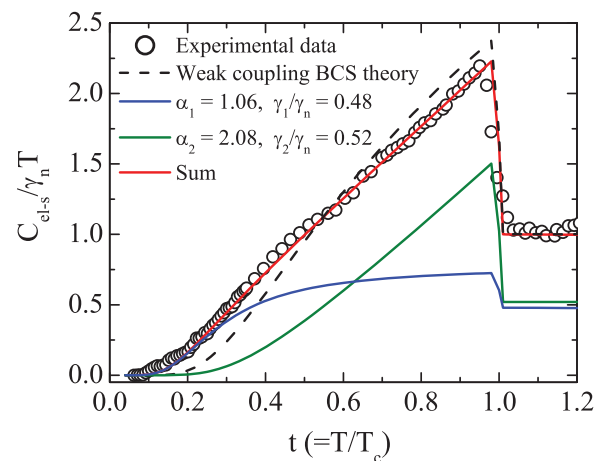


FIG. 4. (Color online) The normalized superconducting electronic specific heat ( $C_{el-s}/\gamma_n T$ ) of  $\text{Ba}_{0.65}\text{Na}_{0.35}\text{Fe}_2\text{As}_2$  as a function of reduced temperature  $t = T/T_c$ . The dashed line represents the theoretical curve based on single-band weak-coupling BCS theory with the  $s$ -wave gap  $\Delta(0)/k_B T_c = 1.76$ , following Eq. (4) and (5). The solid lines represent the curves of the two  $s$ -wave gap models (see text).



coupled single-gap superconductor under a semiempirical approach.<sup>49</sup> This model, however, later had been generalized to explain the specific-heat behavior in multiband, multigap superconductors, i.e., MgB<sub>2</sub>.<sup>50</sup> Following this model, the thermodynamic properties like the entropy  $S$  and  $C$  can be calculated for a system of independent quasiparticles as<sup>49,50</sup>

$$\frac{S}{\gamma_n T_c} = -\frac{6}{\pi^2} \frac{\Delta(0)}{k_B T_c} \int_0^\infty [f \ln f + (1-f) \ln(1-f)] dy, \quad (4)$$

$$\frac{C}{\gamma_n T_c} = t \frac{d(S/\gamma_n T_c)}{dt}, \quad (5)$$

where  $f = [\exp(\beta E) + 1]^{-1}$  and  $\beta = (k_B T)^{-1}$ . The energy of the quasiparticles is given by  $E = \sqrt{[\epsilon^2 + \Delta^2(t)]}$ , where  $\epsilon$  is the energy of the normal electrons relative to the Fermi surface. In Eq. (4), the integration variable  $y = \epsilon/\Delta(0)$ , where  $\Delta(0)$  is the zero-temperature gap magnitude and the scaled gap  $\alpha = \Delta(0)/k_B T_c$  is the only adjustable fitting parameter. The temperature dependence of the gap is determined as  $\Delta(t) = \Delta(0)\delta(t)$ , with  $\delta(t)$  being obtained from the table in Ref. 51. In the case of two gaps, the thermodynamic properties are determined as the sum of contributions from the two gaps, i.e.,  $\alpha_1 [= \Delta_1(0)/k_B T_c]$  and  $\alpha_2 [= \Delta_2(0)/k_B T_c]$  with their respective weights  $\gamma_1/\gamma_n$  and  $\gamma_2/\gamma_n$ , where  $\gamma_1 + \gamma_2 = \gamma_n$ .

Using Eqs. (4) and (5), we first calculate the specific heat  $C_{el-s}/\gamma_n T$  as a function of  $t$  with  $\alpha = 1.76$  for the single-band weak-coupling BCS theory. As evident from Fig. 4, the calculations disagree significantly with our experimental data, where the former is characterized by a higher jump anomaly at  $T_c$ . Moreover, an opposite curvature and different magnitude below and above  $t \approx 0.55$  can be observed for the single-gap model compared to the experimental data. We then calculate  $C_{el-s}/\gamma_n T$ , introducing two gaps and their appropriate weights. Apparently, values  $\alpha_1 = 1.06$  [ $\Delta_1(0) = 2.68$  meV],  $\gamma_1/\gamma_n = 0.48$  and  $\alpha_2 = 2.08$  [ $\Delta_2(0) = 5.27$  meV],  $\gamma_2/\gamma_n = 0.52$ , yield the closest matching with our experimental data (see Fig. 4). Figure 4 also shows the  $C_{el-s}/\gamma_n T$  vs  $t$  plot for an individual  $\alpha$  and its weights.

For the sake of comparison, we have summarized the values of scaled gaps  $\alpha_1$  and  $\alpha_2$  and their respective weights,  $T_c$ ,  $\Delta C_{el}/T_c$ , and  $\gamma_n$  for Ba<sub>0.65</sub>Na<sub>0.35</sub>Fe<sub>2</sub>As<sub>2</sub> along with other hole- and electron-doped 122 materials in Table I. For BNFA, the larger gap  $\alpha_2$  has a higher value than the weak-coupling BCS gap value (1.76), while the smaller one  $\alpha_1$  has a lower value. Although the gap magnitudes are scattered for different compounds within the Ba-122 family, their relative weights exhibit a consistent trend. Upon electron doping the smaller gap has around 30%–40% contribution to the electronic specific heat, whereas for hole-doped compounds both the bands contribute almost equally. While our obtained gap structure for Ba<sub>0.65</sub>Na<sub>0.35</sub>Fe<sub>2</sub>As<sub>2</sub> has qualitative similarity with other hole-doped materials, such as Ba<sub>0.68</sub>K<sub>0.32</sub>Fe<sub>2</sub>As<sub>2</sub>, the gap ratio  $\Delta_2/\Delta_1$  differs significantly (Table I).

In the scenario of an interband pairing model for Fe-pnictides,<sup>52</sup> the gap ratio is predicted as  $\Delta_2/\Delta_1 = \sqrt{N_1/N_2}$ , where  $N_1$  and  $N_2$  are the Fermi-level DOS in the respective bands, and  $\Delta_2/\Delta_1$  is shown to evolve with the effective coupling among the bands. Therefore, one can speculate that the DOS in different bands as well as their coupling modify with K<sup>1+</sup> and Na<sup>1+</sup> doping. Indeed, K<sup>1+</sup> and Na<sup>1+</sup> have

different ionic sizes and electronic configurations, which may contribute differently to these issues. However, the  $\Delta_2/\Delta_1$  ratio implies that  $N_1/N_2$  in Ba<sub>0.68</sub>K<sub>0.32</sub>Fe<sub>2</sub>As<sub>2</sub> is surprisingly about two times higher than in Ba<sub>0.65</sub>Na<sub>0.35</sub>Fe<sub>2</sub>As<sub>2</sub>, which seems to be an unlikely situation with just this kind of dopant variation (see Table I). On the other hand, the fact that  $\gamma_1 \sim \gamma_2 \sim 0.5\gamma_n$  for both compounds implies that both gaps open up at the FS with almost equal DOS, irrespective of the dopant species. These observations probably suggest that the theoretical discussions in Ref. 52 need to include more than two bands. In fact, ARPES results<sup>10,11</sup> strongly hint toward the inclusion of at least four bands (two hole-like and two electron-like bands) opening the superconducting gaps in Ba<sub>1-x</sub>K<sub>x</sub>Fe<sub>2</sub>As<sub>2</sub>. Also, the need for four bands to describe the thermodynamic signatures has been pointed out in theoretical calculations.<sup>48</sup> At the same time, one can clearly see in Table I that within multigap analysis the smaller gap  $\alpha_1$  remains almost close to 1 for all materials (except for the extremely hole-doped case KFe<sub>2</sub>As<sub>2</sub>). However, the larger one  $\alpha_2$ , which appears in the strongly nested inner hole-like and electron-like bands, varies with both the doping elements and their concentration, illustrating that the nesting condition is modified with the doping in Fe-pnictides, which is quite intriguing.

It is worth mentioning here that the employed  $\alpha$  model follows a simple semiempirical approach where the superconducting gap is assumed to have BCS temperature dependence and the interband coupling is not taken into account. Despite such simplification this model has been extensively used to analyze the experimental thermodynamic data for many kinds of materials. While using the  $\alpha$  model, we can categorically show that the present system cannot be described with a single-gap approach; however, to what extent the extracted fit parameters have physical meaning is under question. One, therefore, certainly needs to check other self-consistent models to compare the results. In this scenario, within the framework of the Eliashberg approach for MgB<sub>2</sub> Dolgov *et al.*<sup>53</sup> have shown that the  $\alpha$  model is sufficiently accurate to find the superconducting gap values, although the gap's partial contribution lacks full agreement. Another recently proposed  $\gamma$  model by Kogan *et al.*<sup>54</sup> is also an effective approach that takes into account the interband pairing potential and is successfully tested for two band superconductors, MgB<sub>2</sub> and V<sub>3</sub>Si. Our experimental work calls therefore for a detailed theoretical analysis of our data with these and other appropriate models to fully understand the multigap superconducting nature in Fe-pnictides. In addition, considering the fact that superconducting gaps estimated by using different experimental techniques such as ARPES, PCARS, or muon spin rotation ( $\mu$ SR) exhibit a wide distribution of absolute values,<sup>14</sup> further studies involving specific-heat measurements are required on doped 122 Fe-pnictides with different kinds of doping elements as well as doping concentrations to develop a comprehensive understanding and a generalized view on this matter.

#### IV. CONCLUSIONS

In summary, the electronic properties and superconducting gap structure of the hole-doped 122 Fe-pnictide Ba<sub>0.65</sub>Na<sub>0.35</sub>Fe<sub>2</sub>As<sub>2</sub> are studied by measuring specific heat. A reasonably pronounced anomaly has been found around

$T_c = 29.4$  K. In applied magnetic fields, the transition becomes broadened; however, there is only a minimal decrease in  $T_c$  of about 1.5 K in 90 kOe. Employing an entropy conservation criterion at  $T_c$ , we extract  $\gamma_n = 57.5$  mJ mol<sup>-1</sup> K<sup>-2</sup>, which agrees well with other hole-doped 122 compounds. It is interesting that the temperature-dependent superconducting electronic specific heat cannot be explained within single-band weak-coupling BCS theory. From our analysis we find that the presence of two *s*-wave-like gaps with magnitudes  $\Delta_1(0)/k_B T_c = 1.06$  and  $\Delta_2(0)/k_B T_c = 2.08$  and respective weights of about  $\gamma_1/\gamma_n = 0.48$  and  $\gamma_2/\gamma_n = 0.52$  matches well with our experimental data. Though these results are qualitatively similar to K-doped 122 compounds, on a quantitative level their gap

magnitudes and their ratios are quite different. This calls for further studies on materials with different doping levels to reach a full understanding of the gap structure and related mechanisms.

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\*a.k.pramanik@ifw-dresden.de, ashpramanik@gmail.com

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