CDW order and unconventional s-wave superconductivity in Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O

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Abstract. Due to its anticuprate Ti$_2$O layer and its fascinating phase diagram with a large coexistence area of superconductivity and a density wave phase, the new class of titanium based superconductors attracts great scientific interest. In this paper we report μSR investigation on powder samples of Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O ($x = 0, 0.15, 0.25$). Our results exhibit both the presence of a charge density wave and superconductivity in Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O. The superconducting order parameter, extracted from a vortex state analysis using the numeric Ginzburg-Landau model, is compatible with a s-wave symmetry. In the universal Uemura classification of superconductors this compound is at the verge of unconventional superconductivity.

1. Introduction

The observation of superconductivity with critical temperatures ($T_c$) up to 5.5 K in the Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O [1] raised much interest in the compounds of the CeCr$_2$Si$_2$C-type, which both from the structural and magnetic point of view, may be considered as an unusual superconductor.

The nominal valence state 3$d^1$ of Ti is comparable to 3$d^9$ state of Cu in the cuprates [2, 3]. Compared to the cuprates the oxygen spacing is strongly increased and the parent compound is a metal. In contrast to the planar coordination of Cu in the cuprates, the Ti ions exhibit an extra 90° Ti-Sb-Ti coupling. This effects an octahedral coordination of the Ti atoms between four Sb and two oxygen atoms. In the oxochalcogenides the impact of this structural feature on the order of localized transition metal moments is controversially discussed [4]. For the Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O instead the Fermi surface consists of cylinders [5] enabling density wave (DW) instabilities which were uncovered by ARPES [6] in the related BaTi$_2$As$_2$O. In BaTi$_2$Sb$_2$O such a phase transition was seen by $\chi(T)$ and $\rho(T)$ measurements [1, 2]. NMR investigations [3] assigned it to a charge density wave (CDW) order, although a commensurate spin density wave (SDW) scenario could not be ruled out. The interstitial muon can conclusively discriminated both phenomena.

Numerous approaches have been taken, such as charge doping, structural modification and chemical pressure (table 1), to suppress the DW phase and thus increase the $T_C = 1.2$ K [2] of the parent compound. However, an isovalent Sb/Bi substitution, as reported by Yajima et al. [7], deserves particular attention. It results in a two-dome structure in $T_c$ with two distinct superconducting phases revealing a second mechanism of suppression of superconductivity.

In Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O the sodium substitution leads to effective hole doping within the Ti$_2$Sb$_2$O-layers. The parent compounds from both ends of the phase diagram, BaTi$_2$Sb$_2$O and...
Table 1. Substitution schemes and structural modification of the BaTi$_2$Sb$_2$O. Chemical pressure ("p") as well as hole doping ("h") and interlayers ("IL") can increase $T_C$. If no $T_{DW}$ is stated, the density wave state is no longer traceable. If additionally marked with a star *, $T_{DW}$ went to 0 K (convex) with increasing substitution level, otherwise the signal disappeared at finite temperatures before reaching optimal substitution (concave).

| original | Sb | Sb | Sb | Ba | Ba | Ba | Ba | Ba | Ba |
|---------|----|----|----|----|----|----|----|----|----|
| substituent | none | As | Bi | Sn | Na | Rb | K | (FeAs)$_2$ | (SrF)$_2$ | (SmO)$_2$ |
| mechanism | - | p | p | h | h | h | h | IL | IL |
| $T_{DW}$ [K] | 54 | 200 | -* | 30 | 30 | -* | - | 125 | 198 | 230 |
| $T_{C,\text{max}}$ [K] | 1.2 | - | 4.6 | 2.5 | 5.5 | 5.4 | 6.1 | 21.5 | - | - |

$\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$, show DW transition temperatures of 50 K [7] and 125 K [8, 9], respectively. The sodium compound differs firstly in the nominal interlayer atom count and secondly displays staggered Ti$_2$Sb$_2$O-layers and thus reduced c-axis spacing. However X-ray diffraction pattern [1] place our samples ($x \leq 0.25$) close to the Ba parent compound.

By means of TF-µSR we studied the field and temperature dependence of the flux line lattice to extract superconducting correlation lengths, upper critical fields and the symmetry of the superconducting wave function. For all three Na levels we rule out static magnetic order from our ZF-µSR measurements, and thus a SDW state. This confirms the CDW scenario [7, 10].

2. Experimental
Phase pure Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O polycrystalline specimens were synthesised as described previously [1]. Air sensitive powder samples were filled into kapton sealed bags of sticky tape and measured by means of µSR at the GPS ($x = 0, 0.15$, beamline $\pi$M3.2) and Dolly ($x = 0.25$, beamline $\pi$E1) instruments at the Paul Scherrer Institut (PSI) Villigen, Switzerland. Due to small sample mass of $\approx 20$ mg the spectrometers were run in veto mode. The measurements comprised zero field (ZF) temperature scans in the DW temperature range and transverse field (TF) measurements (except for $x = 0$) up to 0.52 T. The data were analysed using the free software Musrfit [17].

Figure 1. Zero field (ZF) spectra of all substitution levels show no indications of static magnetic order caused by a SDW.

Figure 2. Transverse field (TF) (0.01 T) spectrum at 1.6 K to determine superconducting volume fraction and damping rate $\sigma_{SC}$. 

3. Results and Discussion

Susceptibility measurements indicated superconducting $T_{c, s}$ of 5.5 K and 4.8 K for the $x = 0.15$ and $x = 0.25$ samples. For $x = 0$ a $T_c < 1.5$ K falls below experimental limits [18].

Figure 3. The zero field (ZF) μSR time spectra were described by equation (1). As $\sigma$ and $\lambda_{ZF}$ are highly correlated in this model, $\sigma$ was fitted globally over temperature. This nearly substitution independent damping rate is due to randomly distributed nuclear moments. In the exponential relaxation there is neither a significant feature indicating the $T_{DW}$, nor does $\lambda$ above and below $T_{DW}$ differ. The latter contradicts the SDW scenario.

ZF μSR measurements (Fig. 1) were performed to study the density wave transition. The asymmetry $A(t)$ shows the relaxation of the muon spin polarization due to randomly distributed nuclear moments ($\sigma$) and a exponential relaxation ($\lambda_{ZF}$). It was modelled by the following function:

$$A(t)/A_0 = \left( \frac{1}{3} + \frac{2}{3}(1 - \sigma^2 t^2)e^{-\frac{2\sigma^2 t^2}{T^2}} \right)e^{-\lambda_{ZF}t}$$  \hspace{1cm} (1)

Temperature dependencies of $\sigma$ and $\lambda_{ZF}$ are presented and discussed in Fig. 3. The data is consistent with the CDW scenario, but not with the SDW scenario.

To estimate the superconducting volume fraction $f_{sc}$ and to determine the superconducting order parameters, TF μSR experiments were carried out on the samples $x = 0.15$ and $x = 0.25$ (see Fig. 2). Type II superconductors exhibit a characteristic flux line lattice when exposed to an external magnetic field $B_{ex}$. At temperatures above $T_c$, the muon spins polarized perpendicular to the external magnetic field precesses with the frequency $\gamma B_{ex} = 135.5 \frac{MHz}{T} B_{ex}$. As the field is compressed into flux lines, there will be a unique field distribution $\rho(B_{ex})$ depending on the London penetration depth $\lambda$, the superconducting coherence length $\xi$, and the applied magnetic field $B_{ex}$. Often it is sufficient to treat this distribution in a powder sample as a Gaussian distribution [19] with the second moment $\sigma_B$, which is associated with a damping of the precession signal with the rate $\sigma_{SC} = \gamma \sigma_B$. This most probably is the case for Ba$_{1+x}$Na$_x$Ti$_2$Sb$_2$O$_6$: a Fourier transform of the TF μSR time spectra reveals a paramagnetic line with precession frequency $\omega_0 = \gamma B_{ex}$ and a broadened line corresponding to $f_{sc}$ of the sample.

The μSR spectra were fitted using the following theory for the asymmetry:

$$A(t)/A_0 = f_{sc}\cos(\gamma(B_{ex} + \Delta B)t + \varphi)e^{-\frac{(\sigma_{sc}^2 + \sigma_{nc}^2)t^2}{T^2}} + (1 - f_{sc})\cos(\gamma B_{ex}t + \varphi)e^{-\sigma_{nc}^2 t^2/2}$$  \hspace{1cm} (2)

The damping rate $\sigma_{nc}$ of the normal state was determined for all $B_{ex}$ at 10 K. From this theory the superconducting volume fraction $f_{sc}$ can be deduced (Fig. 4).

Figure 4 indicates that $f_{sc}$ of the $x = 0.15$ sample increases more sharply compared to the one of the $x = 0.25$ sample, where a more gradual enhancement is observed. The field and temperature dependence of $\sigma_{nc}(B, T)$ were further analysed using the numerical Ginzburg-Landau (NGL) model introduced by Brandt [20] (see Fig. 5). Although the often applied analytical approximation for the triangular flux line lattice

$$\sigma_{sc} = \gamma \sigma_B = \gamma \frac{0.172 \Phi_0}{2\pi} \left( 1 - \frac{B}{B_{c2}} \right) \left[ 1 + 1.21 \left( 1 - \sqrt{\frac{B}{B_{c2}}} \right)^3 \right] \frac{1}{\lambda^2}$$  \hspace{1cm} (3)
Figure 4. Superconducting volume fraction $f_{sc}$ extracted from TF data show a less pronounced transition of $x=0.25$ compared to the $x=0.15$ sample.

Figure 5. The complete $\sigma_{SC}(B_{ex},T)$ is well described within the NGL theory [20]. The quadratic flux line lattice (dashed) is to be favoured over the triangular (solid).

gives a reasonable fit to the data for $B \geq 0.015\,\text{T}$, we rather followed Brandt’s more exact three step scheme (for details see [20]). In this numerical model the flux line lattice $B(\vec{R})$ is described in a cosine series and the Fourier coefficients $b_{\vec{R}}$ are modified to fulfil Ginzburg-Landau theory.

\[
B(\vec{R}) = B_{ex} + \sum_{\vec{R} \neq \vec{0}} b_{\vec{R}} \cos(\vec{K} \cdot \vec{R})
\]

From the coefficients $b_{\vec{R}}$ one calculates the second moment $\sigma_B$ of the distribution of magnetic flux $\rho(B)$, which is proportional to the superconducting damping rate $\sigma_{SC}$ measured in the \muSR TF experiment.

\[
\sigma_{sc} = \gamma \sigma_B = \gamma \sqrt{\left\langle (B(\vec{R}) - B_{ex})^2 \right\rangle_{\vec{R}}} = \gamma \sqrt{\frac{1}{2} \sum_{\vec{K}} b_{\vec{K}}^2}
\]

A fitting routine based on Gnu Scientific Library (GSL) [21] was written to extract the effective penetration depth $\lambda_{eff}(T)$ and the upper critical field $B_{c2}(T)$ from the field dependence of $\sigma_{SC}$. In Ginzburg Landau (GL) theory the upper critical field $B_{c2}$ and the superconducting coherence length $\xi$ are related by $\xi^2 = \Phi_0/2\pi B_{c2}$ leading to a coherence length of less than 20\,nm. With the lower critical field $B_{c1,\text{GL}} = \mu_0\Phi_0/4\pi\lambda_{eff}^2 \cdot \ln(1+k)$ calculated from the already deduced data, it can be shown that only two data points lie outside the model range $B_{c1} < B_{ex} < B_{c2}$ (Fig. 5, inset). All superconducting properties are summarized in table 2.

To describe the superfluid density, which is proportional to $\lambda_{eff}^2$, we adopted the isotropic s-wave model [22] from von Rohr [10] and Nozaki [23], who measured at He\textsuperscript{3}-temperatures. The quality of the fit does not depend on the flux line lattice symmetry which was used to extract $\sigma_{SC}$. Superconducting gaps $\Delta_0$ of 0.77(1)\,meV and 0.8(1)\,meV for $x=0.15$ and $x=0.25$ are obtained from the model. These values are in accordance with heat capacity measurements [18].

Although \muSR is usually not the method of choice to determine upper critical fields, the NGL automatically produces these values. The temperature dependence of $B_{c2}$ is sensitive to the choice of flux line lattice symmetry (see Fig. 7). Only the quadratic flux line lattice data points are well described by a WHH model and in line with susceptibility data $B_{c2,\chi}(T)$ [18]. The WHH model yields Maki parameters of 0.6(8) and 1(1) for $x=0.15$ and $x=0.25$ respectively.
This means a Pauli limitation of this superconductor. Although the $\sigma_{SC}(B_{ex}, T)$ data (Fig. 5) is better matched by the quadratic flux line lattice, we stress that our $\mu$SR data alone are not able to discriminate between the different flux line lattice symmetries. In order to validate such a statement, single crystal measurements of the probably anisotropic $\sigma_{SC}$ are essential.

The universal weak coupling BCS behaviour of the gap over critical temperature ratio $\Delta/k_B T_c = 1.764$ is matched by the 25% Na sample (1.9(4)). The more precise value of 1.66(5) for 15% Na lies rather below the BCS prediction, but is still closer to the BCS value than to the value of 1.45 which was extracted by von Rohr for the $x=0.15$ substitution [10].

With the facts accumulated so far the $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$ indeed seems to be an ordinary weak coupled BCS superconductor.

Nevertheless we like to draw attention to Uemura’s universal classification of unconventional superconductors sharing a common condensation mechanism and/or thermodynamic description different from the conventional superconductors [24]. This difference manifests itself in a relatively low Fermi energy. Following Uemura’s formula for the Fermi temperature for two dimensional systems $T_F = \frac{\hbar^2 \pi}{k_B \mu e} \frac{1 + \xi/l}{\lambda^2}$ with the mean free path $l \gg \xi$ and the lattice parameter $c$, $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}$ emerges at the verge of unconventional superconductivity (Fig. 8).
Figure 8. Plot adapted from [25]. Although the universality of the Uemura classification was criticized recently [26] we emphasize its significance to group compounds owing to a common, unusual condensation mechanism and an unconventional thermodynamic description of the superconducting state. The emergence of the strong electron-phonon coupled MgB$_2$ in this plot illustrates, that phonon mediated pairing is no criteria of exclusion within this classification. The vicinity of Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O to unconventional superconductors is rather attributed to the multi-band electron [5] and layered crystal structure (as in MgB$_2$), to the presumably important 3d-electron correlations and to the competing CDW order (the latter two similar in NbSb$_2$).

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References
[1] Doan P, Gooch M et al. 2012 J. Am. Chem. Soc. 134 16520–16523
[2] Yajima T, Nakano K, Takeiri F et al. 2013 J. Phys. Soc. Jpn. 82 013703
[3] Kitagawa S, Ishida K, Nakano K, Yajima T and Kageyama H 2013 Phys. Rev. B 87 060510
[4] Fuwa Y, Wakeshima M and Hinatsu Y 2010 J. Phys.: Condens. Matter 22 346003
[5] Singh D J 2012 New J. Phys. 14 123003
[6] Xu H C, Xu M, Peng R, Zhang Y, Ge Q Q, Qin F, Xia M, Ying J J et al. 2014 Phys. Rev. B 89 155108
[7] Yajima T, Nakano K, Takeiri F, Nozaki Y, Kobayashi Y and Kageyama H 2013 J. Phys. Soc. Jpn. 82 033705
[8] Adam A and Schuster H U 1990 Z. Anorg. Allg. Chem. 584 150–158
[9] Liu R H, Tan D, Song Y A, Li Q J, Yan Y J, Ying J J et al. 2009 Phys. Rev. B 80 144516
[10] von Rohr F, Schilling A, Nesper R, Baines C and Bendele M 2013 Phys. Rev. B 88 140501
[11] Wang X, Yan Y, Ying J, Li Q, Zhang M, Xu N and Chen X 2010 J. Phys.: Condens. Matter 22 075702
[12] Nakano K, Yajima T, Takeiri F, A Green M, Hester J, Kobayashi Y and Kageyama H 2013 J. Phys. Soc. Jpn. 82 074707
[13] von Rohr F, Nesper R and Schilling A 2014 Phys. Rev. B 89 094505
[14] Pachmayr U and Johrendt D 2013 Solid State Sci. 28 21–34
[15] Sun Y L, Ablimit A, Bao J K, Jiang H, Zhou J and Cao G H 2013 Sci. Tech. Adv. Mater. 14 055008
[16] Liu R, Song Y, Li Q, Ying J, Yan Y, He Y and Chen X 2010 Chem. Mater. 22 1503–1508
[17] Suter A and Wojek B 2012 Physics Procedia 30 69–73
[18] Gooch M, Doan P, Tang Z, Lorenz B, Guloy A M and Chu P C 2013 Phys. Rev. B 88 064510
[19] Maeter H 2012 Muon spin relaxation and rotation of iron-based superconductors Ph.D. thesis TU Dresden
[20] Brandt F H 2003 Phys. Rev. B 68 054506
[21] Galassi M et al. 2011 Gnu Scientific Library: Reference Manual, Edition 1.15, for GSL Version 1.15
[22] Prozorov R 2008 Supercond. Sci. Technol. 21 082003
[23] Nozaki Y, Nakano K, Yajima T, Kageyama H, Frandsen B, Liu L et al. 2013 Phys. Rev. B 88 214506
[24] Uemura Y, Le L, Luke G, Sternlieb B, Wu W, Brewer J et al. 1991 Phys. Rev. Lett. 66 2665–2668
[25] Khasanov R, Luetkens H, Amato A, Klauss H H et al. 2008 Phys. Rev. B 78 092506
[26] Dordevic S, Basov D and Homes C 2013 Scientific Reports 3 1713