Possible singlet-to-triplet pairing transition in $Na_xCoO_2 \cdot yH_2O$

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We present precise measurements of the upper critical field (H_{c2}) in the recently discovered cobalt oxide superconductor. We have found that the critical field has an unusual temperature dependence; namely, there is an abrupt change of the slope of $H_{c2}(T)$ in a weak-field regime. In order to explain this result we have derived and solved Gor'kov equations on a triangular lattice. Our experimental results may be interpreted in terms of the field-induced transition from singlet to triplet superconductivity.

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I. INTRODUCTION

The recent discovery of superconductivity in $Na_xCoO_2 \cdot yH_2O$,[1] may provide a unique insight into the mechanisms, which determine superconducting properties of transition metal oxides. Although the superconducting transition temperature, T_c, is much lower than T_c's in cuprate superconductors, both system share many common features. Co oxide becomes superconducting after hydration that significantly enhances the distance between CoO_2 layers. This suggests crucial importance of the dimensionality. In particular, a quasi-two-dimensional character of Co oxide shows up in the resistivity measurements. Above the transition temperature, the in-plane resistivity is three orders of magnitude less than out-of-plane one.[2] Similarly to cuprates the Co-based superconductor represents a strongly correlated system. The strong correlations may be responsible for a nonmonotonic doping dependence of T_c. Namely, the critical temperature is maximal for a particular carrier concentration and decreases both for overdoped and underdoped materials.[3]

However, in contradistinction to cuprates, CoO_2 layers have a form of a triangular lattice. This feature may be responsible for magnetic frustration and unconventional symmetry of the superconducting order parameter. Investigations of the pairing symmetry with the help of nuclear magnetic resonance (NMR) (Ref. 4) and nuclear quadrupole resonance (NQR) (Ref. 5) lead to contradictory results. In particular, the presence of nodes in the superconducting gap remains an open problem. It is also unclear whether superconductivity originates from singlet or triplet pairing. Theoretical investigations do not lead to firm conclusions. It has been shown that the resonating valence bond state (RVB) may be realized in the t-J model on a triangular lattice,[6] provided $t > 0$. This may suggest RVB as a straightforward explanation of superconductivity in the Co oxides.[7] However, it is interesting that in addition to singlet superconductivity, there is a region of triplet pairing in the phase diagram proposed in Ref. 7. Moreover, LDA calculations suggest that the ground state of the parent system $NaCo_2O_4$ may be ferromagnetic.[8] Recent density functional calculations carried out for $Na_xCo_2O_4$ predict an itinerant ferromagnetic state that, however, competes with a weaker antiferromagnetic instability.[9] Triplet superconductivity has also been postulated on the basis of symmetry considerations combined with analysis of experimental results.[10]

Therefore, the symmetry of the superconducting order parameter remains an open problem and both singlet and triplet pairings should seriously be taken into account. In particular, it is possible that singlet and triplet types of superconductivity compete with each other. In such a case an external magnetic field may favor triplet pairing, due to the absence of the Zeeman pair breaking mechanism in this state. This should be visible in the temperature dependence of the upper critical field, H_{c2}. In order to verify this possibility we carry out precise measurements of H_{c2}. The obtained results clearly indicate unconventional temperature dependence of H_{c2}, that cannot be described within the Werthamer-Helfand-Hohenberg (WHH) theory.[11] The experimental data are compared with theoretical results obtained from the solution of the Gor'kov equations on a triangular lattice. These results may be interpreted in terms of a field-induced transition from singlet to triplet superconductivity and suggest that phase sensitive measurements to distinguish this from other possible interpretations would be of great interest.

II. EXPERIMENTAL RESULTS

The measurements have been carried out on $Na_{0.3}CoO_2 \cdot 1.3H_2O$. $Na_{0.7}CoO_2$ (0.5 g) was stirred in 20 ml of a $40 \times Br_2$ solution in acetonitrile at room temperature for 4 days ("$1\times$" indicates that the amount of Br_2 used is exactly the amount that would theoretically be needed to remove all the Na from $Na_{0.7}CoO_2$). The product was washed copiously with acetonitrile, followed by water and air-dried. After air-drying, the product was kept in a sealed container with 100% relative humidity for 2 days to obtain the hydrated superconductor.

All the magnetic measurements were performed using dc magnetometer/ac susceptometer MagLab 2000 System (Oxford Instruments Ltd.). There is only one superconducting phase transition in the sample and there is no coexistence of phases with different critical temperatures or critical fields. It
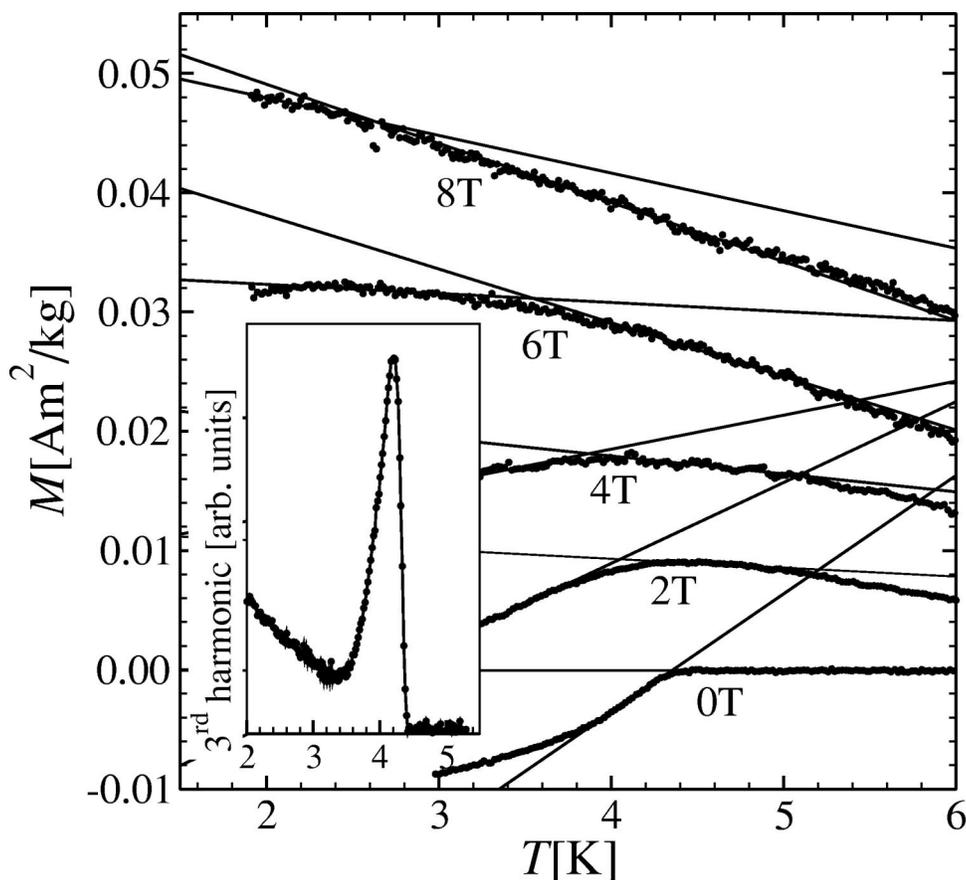
FIG. 1. Temperature dependence of mass magnetization $M(T)$ for various magnitudes of magnetic fields. For clarity of the figure the $M(T)$ curves are offset, except the one for 0T. The inset presents temperature dependence of the third harmonic susceptibility.

has been well confirmed by a single peak in a temperature dependence of magnitude of the third harmonic ac susceptibility (see the inset in Fig. 1). For third harmonic measurements the ac magnetic field of frequency $f=1$ kHz and amplitude $H_{ac}=10^{-4}$ T was applied. For the dc measurements we have applied magnetic fields up to 9 T. The temperature was stepped in the range about 3–6 K in the case of low and moderate magnetic fields and in the range about 2–6 K for the highest fields. The size of the step was 20 mK and the temperature was stabilized during each measurement with the accuracy 2 mK. A set of typical $M(T)$ curves recorded for applied fields of 0, 2, 4, 6, and 8 T is shown in Fig. 1. Except the case of lowest magnetic fields the magnetization is positive in the whole temperature range. It is due to the domination of ferromagnetic and/or paramagnetic contributions in the total magnetization at higher fields. The superconducting transition manifests itself as a downturn in $M(T)$ at low magnetic fields, whereas at the higher fields only the change in the slope in $M(T)$ is observed. This enabled a simple determination of the critical temperature; namely, T_c was determined from the intersection of the two straight-lines that fit relevant linear regimes (see Fig. 1). The zero-field critical temperature determined in this way is $T_c(0) = 4.345 \pm 0.015$ K. The results of the measurements are presented in Fig. 2 in equivalent form as $H_{c2}(T)$.

Close to $T_c(H=0)$ one can expect that the Ginzburg-Landau theory gives accurate results and, therefore, temperature dependence of H_{c2} should be linear. In cuprate superconductors H_{c2} shows unconventional temperature

dependence.[12,13] Close to $T_c(H=0)$ $H_{c2}(T)$ is almost linear and, then, the curvature smoothly increases with the decreasing temperature. However, as can be inferred from Fig. 2, this is not the case for $Na_xCoO_2 \cdot yH_2O$. For $1T \lesssim H \lesssim 3T$ the experimental data can be fitted very well by a linear function. However, such a fit deviates from experimental points for weaker magnetic field. Similar temperature dependence of H_{c2} has been obtained, e.g., from the specific heat measurements.[14] For $H \lesssim 3T$ the experimental data presented in Fig. 2, as well as those reported in Ref. 14, can be fitted by
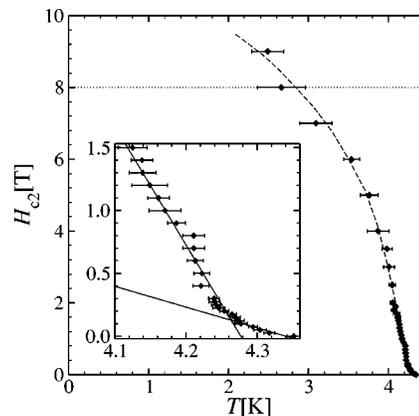

FIG. 2. Experimental data for $H_{c2}(T)$. The horizontal line shows the Clogston-Chandrasekhar limit, whereas the line connecting experimental points is only a guide for the eye. The inset shows $H_{c2}(T)$ in the low field regime fitted by two lines.

two linear functions. In our case they are: $H_{c2}(T)$ =7.4−1.7 T in the weak field regime and $H_{c2}(T)$ =40−9.4 T for stronger magnetic field. Using the WHH formula,[11] $H_{c2}(0) \simeq 0.7 T_c (dH_{c2}/dT)|_{T_c}$, one estimates corresponding values of $H_{c2}(0)$'s equal to 5.2 T and 28 T, respectively. Such a behavior may originate from competition between two superconducting order parameters with close transition temperatures but different temperature dependencies of H_{c2}. Singlet and triplet order parameters are possible candidates due to the absence of Zeeman pair breaking in the latter case. $H_{c2}(0)$ obtained from the WHH formula in the strong field regime is beyond the Clogston-Chandrasekhar (CC) limit. $H_{c2}(0)$'s reported in Ref. 15 and estimated from Ref. 14 are even higher. Although, the extrapolated $H_{c2}(0)$ may be overestimated, our experimental data clearly show that H_{c2} exceeds the CC limit already for $T \simeq 0.6\ T_c$. The large slope of $H_{c2}(T)$ suggests that even in the case of renormalization of the paramagnetic pair breaking mechanism (e.g., similar to that in the strong-coupling electron-phonon approach[16]) $H_{c2}(0)$ should be beyond the CC limit. This speaks in favor of triplet superconductivity. On the other hand, $H_{c2}(0)$ estimated from the low field data does not exceed CC limit. Therefore, superconductivity in a weak magnetic field may originate from the singlet pairing. In the following we show that this tempting interpretation of experimental data remains in agreement with theoretical results obtained from the numerical solution of the Gor'kov equations. Our fit neglects a positive curvature of $H_{c2}(T)$ that occurs for $H \lesssim 0.9$ T. At the end of this paper, we discuss possible origins of this feature.

III. THEORETICAL APPROACH TO THE UPPER CRITICAL FIELD

In order to calculate the upper critical field we consider a triangular lattice immersed in a uniform perpendicular magnetic field:

$$H = \sum_{\langle ij \rangle \sigma} t_{ij} e^{i\theta_{ij}} c_{i\sigma}^\dagger c_{j\sigma} - \mu \sum_{i,\sigma} c_{i\sigma}^\dagger c_{i\sigma} - g\mu_B H_z \sum_i (c_{i\uparrow}^\dagger c_{i\uparrow} - c_{i\downarrow}^\dagger c_{i\downarrow})$$
$$+ V^s \sum_{\langle ij \rangle} (\Delta_{ij} c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger + \text{H.c.}) + V^t \sum_{\langle ij \rangle} \sum_{\sigma_1, \sigma_2 = \uparrow \downarrow} (\Delta_{ij}^{\sigma_1 \sigma_2} c_{i\sigma_1}^\dagger c_{j\sigma_2}^\dagger$$
$$+ \text{H.c.}). \quad (1)$$

t_{ij} is the hopping integral between the sites i and j in the absence of magnetic field and θ_{ij} is the Peierls phase factor, responsible for the diamagnetic response of the system:

$$\theta_{ij} = \frac{2\pi}{\Phi_0} \int_i^j A \cdot dl, \quad (2)$$

where $\Phi_0 = hc/e$ is the flux quantum. The chemical potential μ has been introduced in order to control the carrier concentration. In the Hamiltonian (1)

$$\Delta_{ij} = \langle c_{i\uparrow} c_{j\downarrow} - c_{i\downarrow} c_{j\uparrow} \rangle \quad (3)$$

and

$$\Delta_{ij}^{\uparrow\downarrow} = \langle c_{i\uparrow} c_{j\downarrow} + c_{i\downarrow} c_{j\uparrow} \rangle, \quad (4)$$
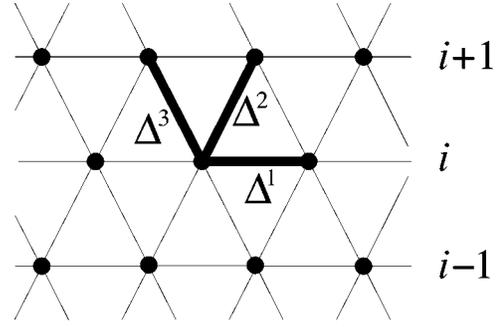

FIG. 3. Order parameters for superconductivity on a triangular lattice. Such a set of order parameters is introduced in each pairing channel, i.e., for Δ, $\Delta^{\uparrow\downarrow}$, $\Delta^{\uparrow\uparrow}$, $\Delta^{\downarrow\downarrow}$.

$$\Delta_{ij}^{\uparrow\uparrow} = \langle c_{i\uparrow} c_{j\uparrow} \rangle, \quad (5)$$

$$\Delta_{ij}^{\downarrow\downarrow} = \langle c_{i\downarrow} c_{j\downarrow} \rangle \quad (6)$$

denote the pairing amplitudes in singlet and triplet channels, respectively.

In order to determine the upper critical field we follow the procedure introduced in Refs. 17 and 18. Namely, we diagonalize the kinetic part of the Hamiltonian [the first term in Eq. (1)] by introducing a new set of fermionic operators. In the Landau gauge $A = (-H_z y, 0, 0)$ this set of fermionic operators is determined by a one-dimensional eigenproblem known as the Harper equation. We restrict further considerations to the nearest-neighbor hopping, i.e., $t_{ij} = t$ for the neighboring sites i, j and 0 otherwise.

Using the solutions of the Harper equation we write down a self-consistent equation for the gap functions. Magnetic field breaks the translational symmetry and, therefore, the order parameters are site dependent. However, in the chosen gauge they depend on the y coordinate only. As the superconductivity develops on the triangular lattice, at each site we introduce three order parameters $(\Delta^1, \Delta^2, \Delta^3)$ in each pairing channel, i.e., for Δ, $\Delta^{\uparrow\downarrow}$, $\Delta^{\uparrow\uparrow}$, $\Delta^{\downarrow\downarrow}$ (see Fig. 3). In order not to assume any particular pairing symmetry we consider these order parameters as independent quantities. In the following we do not assume any particular orbital symmetry of the pair state. However, independently of this symmetry all these order parameters vanish at T_c. Therefore, the gap equation can be expressed with the help of three vectors $\Delta^{1,2,3}$, where $\Delta^a = (\Delta_1^a, \Delta_2^a, \dots)$. The lower index enumerates rows of the lattice sites, whereas the upper one indicates the direction of the bond, as depicted in Fig. 3. H_{c2} is defined as a field, at which all components of these vectors vanish. This can be determined from the linearized version of the gap equation that is of the following form:

$$\begin{pmatrix} \Delta^1 \\ \Delta^2 \\ \Delta^3 \end{pmatrix} = (\mathcal{M}) \begin{pmatrix} \Delta^1 \\ \Delta^2 \\ \Delta^3 \end{pmatrix}. \quad (7)$$

For the sake of brevity we do not present an explicit form of $\mathcal{M}$. This matrix can be expressed with the help of the Cooper pair susceptibility and eigenfunctions obtained from the Harper equation.
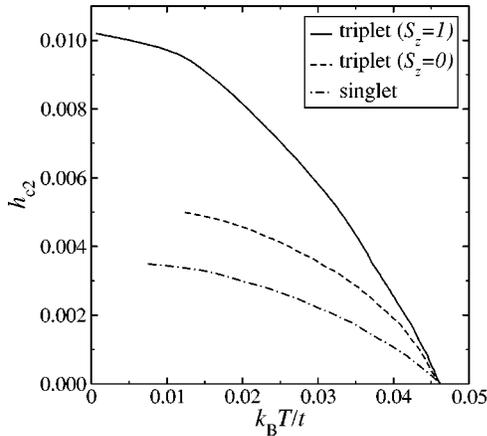
FIG. 4. Numerical results for $h_{c2}(T)$. Presented results have been obtained for occupation number $n=0.95$ and for $V^s=0.55t$, $V^t=0.75t$.

The temperature dependence of H_{c2} has been obtained from Eq. (7) for singlet and triplet superconductivity. In the latter case we have investigated separately the paired states $|\downarrow\downarrow\rangle$, $1/\sqrt{2}\,(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle)$, and $|\uparrow\uparrow\rangle$. We refer to these states by the corresponding spin projection $S_z=-1,0,1$, respectively. These states are affected by the magnetic field in different ways due to the Zeeman coupling. In the case of equal-spin-pairing this coupling is almost ineffective as it leads to a renormalization of the chemical potential only $\mu \to \tilde{\mu} = \mu \pm 1/2 g \mu_B H_z$.

Figures 4 and 5 show the numerical results obtained for 150×150 cluster. In particular, in Fig. 5 we have chosen the occupation number that is close to the experimentally determined optimal doping. We present a reduced magnetic field $h=2\pi\Phi/\Phi_0$, where Φ_0 is the flux quantum and Φ is the magnetic flux through the lattice cell. When the zero-field transition temperatures for singlet and triplet pairings are of comparable magnitudes, the slope of $H_{c2}(T)$ is much larger for triplet superconductivity. As a result, the triplet superconductivity is characterized by much larger $H_{c2}(T=0)$. It is interesting that this feature remains valid also for triplet pair-
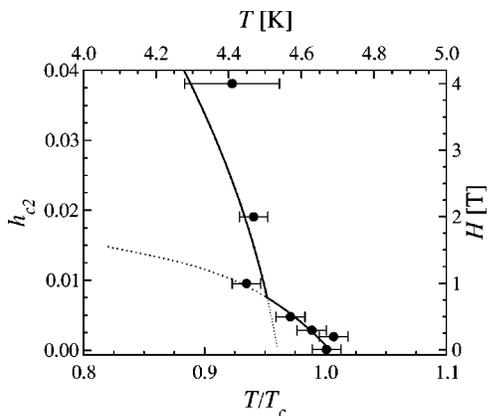

FIG. 5. Numerical results for $h_{c2}(T)$. We have assumed the model parameters $n=0.67$ and $V^s=V^t=0.7t$. For these model parameters $kT_c \simeq 0.2t$. The experimental points have been taken from Ref. 14.

ing with $S_z=0$ that is affected by the Zeeman pair breaking (see Fig. 4). As expected, the highest value of the upper critical field is obtained for the triplet equal-spin-pairing. Comparing Figs. 4 and 5 one can see that the above statements on the slope of $H_{c2}(T)$ hold in a wide range of the model parameters. However, due to limitation of the cluster approach it is difficult to perform numerical calculations at very low temperatures.[17] From Figs. 4 and 5 follows that experimental data are qualitatively reproduced when $T_c(H=0)$ for triplet superconductivity is slightly less than the transition temperature for the singlet one. Then, sufficiently strong magnetic field leads to a transition from singlet to triplet superconductivity that shows up in a change of the slope of $H_{c2}(T)$.

The external magnetic field affects the relative phase of the order parameter in different directions presented in Fig. 3. According to Eq. (2) this phase can change from site to site and, therefore, it is impossible to determine globally the type of the symmetry of the energy gap. However, we have found that for singlet pairing $T_c(H=0)$ is exactly the same as transition temperature obtained for d_1+id_2 symmetry, according to the notation in Ref. 7. On the other hand, for the triplet pairing $T_c(H=0)$ corresponds to that for the f-wave pairing when $n \lesssim 1$ and p_x+ip_y symmetry for larger occupation number. The exact position of the boundary between both the triplet solutions depends on the pairing potential.

IV. DISCUSSION AND CONCLUSIONS

Our linear fit to the experimental data in the intermediate field regime seems to be very accurate, strongly supporting the triplet pairing. Even stronger evidence comes from the presence of superconductivity above the CC limit. However, at weak field there exists also another possibility: $H_{c2}(T)$ for the field less than approximately 0.9 T can be fitted by a concave curve. Similarity between $Na_xCoO_2 \cdot yH_2O$ and high-T_c superconductors may suggest a common mechanism that leads to the positive curvature of $H_{c2}(T)$. This also speaks in favor of a singlet pairing in this regime. In such an approach the singlet-triplet transition takes place at slightly higher field, $H \approx 0.9$ T. From a theoretical point of view the upward curvature of $H_{c2}(T)$ can occur for instance in: extremely type II superconductors described by the boson-fermion model,[19] the systems with a strong disorder sufficiently close to the metal-insulator transition,[20] the disordered superconductors due to mesoscopic fluctuation,[21] Josephson tunneling between superconducting clusters,[22] in a mean-field-type theory of H_{c2} with a strong spin-flip scattering,[23] and due to a reduction of the diamagnetic pair-breaking in the stripe phase.[24] Other theoretical approaches to this problem include, e.g., the superconductivity with a mixed symmetry $(s+d)$ order parameter[25] and Bose-Einstein condensation of charged bosons.[26]

$H_{c2}(T)$ obtained from the resistivity measurements[27] is lower than presented here and, e.g., in Refs. 14 and 15. In particular, it is lower than $H_{c2}(T)$ obtained from magnetization measurements on quasisingle crystals.[28] This discrepancy remains unexplained. One of possible explanations is

that it originates from the presence of lattice defects, that for short coherence length superconductors form Josephson junctions. These junctions affect the resistivity measurements much stronger than the magnetization ones.

To conclude, we have measured the temperature dependence of the upper critical field in $Na_{0.3}CoO_2 \cdot 1.3H_2O$ and we have found an interesting feature: namely, an abrupt change of slope of $H_{c2}(T)$ in a weak-field regime. This feature is in qualitative agreement with results reported in Ref. 14. Moreover, such a bend in a weak field regime is visible also in other magnetization measurements,[15] in specific heat measurements[14] as well as in resistivity measurements [see Fig. 4(a) in Ref. 27]. In order to explain the origin of such a behavior we have solved Gor'kov equations on a triangular lattice for singlet and triplet types of pairing. Our experimental results are consistent with a scenario of competing singlet and triplet superconductivity. Within such an approach magnetic field induces a transition from singlet to triplet superconductivity that shows up in a change of slope of $H_{c2}(T)$: in a weak magnetic field the singlet pairing takes place and sufficiently strong magnetic field drives the system into the triplet state. Recently, a field-induced transition between various types of singlet superconductivity has been proposed to take place in cuprates[29] (an occurrence of a minor id_{xy} component of the order parameter).

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